THE POLYMERISATION OF ACRYLONITRILE .

A thesis submitted to the University of Glasgow in accordance with the regulations for the award of the degree of Doctor of Philosophy.

by

Samuel A. McIntosh, B.Sc.

Department of Chemical Technology,

Royal College of Science & Technology,

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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

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The following preliminary note contains details of one of the experimental methods used in this thesis.

A Modified Rotating Sector Method of Measuring Kinetic Chain Lifetimes.

Bengough, McIntosh, & Thomson, Nature, 1959, 184, 266.

SUMMARY.

In part I of this thesis, the kinetics of the photoinitiated polymerisation of acrylonitrile, in bulk, in a precipitating medium, and in solution, have been studied and compared. Polyacrylonitrile is insoluble in the monomer and the precipitating medium consisted of appropriate mixtures of acrylonitrile (AN) and dimethylformamide (DMF). At higher molar ratios of DMF:AN, the polymer produced remained in solution. α,α'-azo-bis-iso-butyronitrile was used as the photosensitiser in all cases.

The rate dependences on monomer and initiator were found. For solution polymerisation, the following rate relationship was found to hold up to 10% conversion:

$$\text{Rate} = K [C]^{0.5} [M]^{1.0} \qquad (1)$$

where K is a constant of proportionality, [C] is the concentration of the initiator, and [M] is the monomer concentration. Two separate rate relationships were found for the bulk polymerisation. In the very early stages of the reaction, the kinetic scheme approximated closely to that shown in equation (1). At later stages of the reaction, the following relationship was obtained:

$$\text{Rate} = K\,[C]^{0.56 - 0.65}\,[M]^{\sim 2.5} \qquad (2)$$

The initiator exponent was found by using AIBN as a thermal initiator at 60°C.

These differences have been explained on the basis of an occlusion theory.

The rate of initiation of the polymerisation has been evaluated using radical scavenging and inhibition techniques involving reactions with α,α'-diphenyl-β-picrylhydrazyl (DPPH). It was found that the rate of initiation, as determined by this method, was dependent on the nature of the solvent medium. Hydrogen abstraction reactions, involving the production of the α,α'-diphenyl-β-picrylhydrazine, have been postulated to explain these results.

The velocity coefficients for the transfer reactions of DMF and bromotrichloromethane (BTCM) with the growing radical

were found to be 0.135 and 2.03 $l.mol.^{-1}sec.^{-1}$ respectively. The former is of the correct order of magnitude but the latter is lower than corresponding values reported in telomerisation studies.

The overall energy of activation was evaluated over a wide range of monomer concentrations, using AIBN as a thermal initiator. For the lower monomer concentrations, the average value obtained was 21.8 Kcal./mol. whilst higher values (~25 Kcal./mol.) were found in reaction mixtures containing more than 12.82 mol./l. of acrylonitrile. It is thought that these higher values may be due to the increased occlusion of the growing radicals.

The velocity coefficients for propagation (k_2) and termination (k_4) have been determined using non-stationary state methods. The values obtained over the heterogeneous range were constant and gave average values of:

$$k_2 = 3.92 \times 10^2 \quad ; \quad k_4 = 3.74 \times 10^7$$

The results obtained in the homogeneous region were also constant, the average values being:

$$k_2 = 2.82 \times 10^3 \quad ; \quad k_4 = 2.11 \times 10^9$$

The values found for the velocity coefficients for propagation

and termination therefore show distinct differences dependent on whether the growing radical is in the liquid or solid phase. This is a more fundamental factor than was envisaged in the earlier theories on the polymerisation of acrylonitrile.

Part II of this thesis concerns the preliminary investigation of the photoinitiated reaction between ferric chloride and acrylonitrile. The experimental difficulties involved are discussed and a method of estimating ferrous iron in the presence of excess dimethylformamide is given.

I N D E X .

Part I.

PART I.

The kinetics of the α,α'-azo-bis-isobutyronitrile initiated polymerisation of acrylonitrile.

CHAPTER 1.

INTRODUCTION.

Observations on the polymerisation of readily polymerisable vinyl monomers date back approximately to the first recorded isolation of the monomer. In 1839, Simon[1] reported the conversion of styrene to a gelatinous mass and Berthelot[2] later applied the term "polymerisation" to this process.

In 1910, Stobbe and Posnjak[3] concluded that polystyrene was a "colloidal body" since the boiling point elevation of its solutions was negligible. Lebedev[4,5] was one of the first to recognise that the polymers had a high molecular weight but his suggested mechanism for the growth process resembled a process of intermolecular association. At this stage, however, prevailing

opinion favoured rings of moderate size for vinyl and diene polymers similar to those suggested by Harries[6].

The first major advance in the subject occurred as a result of the paper published by Staudinger[7] in which he suggested a chain mechanism, the formulae of the intermediates being written with free valences at both ends of the molecule. He considered that activation of the monomer molecule resulted in the opening of the double bond and that the activated molecule then reacted with successive monomer units to give intermediates similar to those described above. He assumed also that termination occurred by deactivation of the radical by virtue of its long chain length. These discussions, however, were rather vague and imprecise and the first complete free radical mechanism for a polymerisation reaction was given by Taylor & Jones in 1930[8].

Another mechanism was suggested by Whitby & Katz[9] who, although accepting the idea of linear polymeric molecules, did not agree with Staudinger's concept of free radical intermediates. They postulated a mechanism involving successive hydrogen transfer between a polymeric molecule and the vinyl monomer. Even in 1936, at a symposium on polymerisation[10], both the free radical and stepwise hydrogen transfer mechanisms were discussed.

Thus, the theory that polymerisations could occur by free

radical chain mechanisms was not universally accepted for almost another decade. It was finally accepted when it was shown that polymerisations could be initiated by substances which were known to give radicals on decomposition or by photo - excitation. Detailed kinetic analyses of vinyl polymerisations also gave results which could be correlated to a radical mechanism. This latter evidence was slow in coming forth since the influence of impurities on a reaction involving radical intermediates was not fully appreciated.

The normal kinetic scheme is now taken to be:

$$C \rightarrow C\cdot \qquad \ldots(1.1)$$

$$C\cdot + M \rightarrow R_1 \qquad \ldots(1.2)$$

$$R_n + M \rightarrow R_{n+1} \qquad \ldots(1.3)$$

$$R_n + R_m \rightarrow \text{Polymer} \qquad \ldots(1.4)$$

where C and M are molecules of initiator and monomer respectively, R represents a growing radical chain, the subscripts refer to the number of monomer units in the chain, and C· is a radical derived from the initiator. (N.B. In this thesis, the terms radical and free radical are synonomous). Equations (1.1) and (1.2) are the initiation steps of the polymerisation whilst equations (1.3) and (1.4) are the propogation and termination reactions. This

scheme gives the following rate equation:

$$\text{Rate} = k_2 [C]^{0.5} [M]^{1.0} \qquad \ldots(1.5)$$

where k_2 is the velocity coefficient for the propagation step.

The assumptions involved in deriving this simplified scheme are discussed in chapter 5.

It is only in recent years that the study of the polymerisation of acrylonitrile has been attempted. The first detailed results were published in 1953 by Bamford and co-workers[11,12] and by Prévot-Bernas[13]. Since then, this reaction has been closely studied by many workers, and the published results fall into two main categories. One deals with the bulk polymerisation of the monomer (the polymer being insoluble in acrylonitrile) and the other deals with the polymerisation of acrylonitrile in solution.

The bulk polymerisation of acrylonitrile shows many deviations from the normal characteristics of vinyl polymerisations whilst the solution polymerisation seems to accord, more or less, with the above kinetic scheme. Bamford & Jenkins[12] have claimed that the rate of polymerisation of acrylonitrile in bulk polymerisation increased with the duration of the reaction in both thermally and photochemically initiated reactions. Thomas and Pellon[14], however, have stated that this acceleration is only apparent up to 3%

conversion, the rate then becoming linear.

Also for heterogeneous polymerisation, the reported rate dependences on monomer concentration vary from 1.0[15] to 3.0[16] and on initiator concentration, from 0.5[17] to 1.0[15,16].

Linear rate - time relationships have been obtained for the solution polymerisation of acrylonitrile in dimethylformamide[12]. In this case, the reported rate dependences are within a narrower range, the rate dependence on initiator varying from 0.50[18,19] to 0.59[20] and, on monomer concentration, from 1.0[21] to 1.7[19].

Several values for the velocity coefficients for propagation (k_2) and termination (k_4) have been suggested. For bulk polymerisation, the values reported vary from 24[22] to 127[23] for k_2 and from 2.3×10^7 , [22] to 1.2×10^7 , [23] for k_4 at 50°C and 25°C respectively. The corresponding values, obtained at 60°C, in solution polymerisation were 2,458 and 9.80×10^8 , [24].

Various explanations have been given for the anomalous kinetics of the bulk polymerisation of acrylonitrile. Thomas & Pellon[14] based their kinetic scheme on an additional first order termination step involving termination of a radical by complete burial in a polymer aggregate. This would explain both the high intensity exponents obtained and the characteristic accelerating rate. This theory has been refuted by Bamford & Jenkins[25] since the

number of radicals which would have to be trapped is vastly in excess of that found by experimental means.

The explanation put forward by Durup & Magat[22] claimed that, although termination between polymer radicals was unlikely, bimolecular termination might occur with primary radicals. This implied that, if no primary radicals were present, propagation would continue at the same rate until all the monomer had been consumed, since there would then be no termination reaction. This has been tested experimentally in a photoinitiated reaction using di-tert-butyl peroxide as sensitiser[26]. When the irradiation was cut off, the rate fell rapidly to a low value and thus this theory cannot be applied to the polymerisation.

The most widely accepted theory at present is due to Bamford, Barb, & Jenkins[11] and this postulates occlusion of radicals. This theory is based mainly on the supposition that many, if not all, of the polymer radicals are precipitated from the liquid phase. These radicals are presumed to be tightly coiled since the medium is a non-solvent for the polymer. This type of coiled radical would have a reduced activity due to the high probability that the radical end would be occluded in the coils. If this coiled radical coalesces with a particle of dead polymer, then its reactivity would be further reduced. It is claimed that

coiling has little significance in swollen polymer compared to its importance in the non-swollen polymer but, in both cases, coalescence is assumed to have the greatest effect on the reactivity of the radicals[25].

This theory would involve a lowering of the velocity coefficients for all reactions which take place with the radical chain (i.e. propagation, transfer, and termination). The degree to which each of these coefficients would be affected would depend on the rate of diffusion of the other reactant into the polymer aggregate. Bimolecular termination would obviously be affected more than either propagation or transfer reactions and could only occur between two occluded radicals when both the radical ends were on the surface of the polymer aggregates.

Another termination reaction which could be envisaged involves mutual termination between mobile radicals. These could be of two types:

(a) Radicals derived directly from the primary initiating radicals but which have not coalesced with any polymer particles, or

(b) Short chain radicals formed by transfer between monomer or solvent and an occluded radical. Due to their size, the radicals should then be able to diffuse out of the polymer aggregate.

The long-lived activity of the photopolymer of acrylonitrile in the presence of monomer at low temperatures,[27-29] together with the low rate of reaction observed, shows that the formation of mobile radicals by chain transfer to monomer occurs at a negligible speed.

Thus, it is claimed, the characteristic behaviour of heterogeneous systems is determined both by the number of polymer particles present and by their total weight. As the polymerisation progresses, the number of polymer particles present, and their average size, increases thus giving a decrease in the termination coefficient which in turn gives an accelerating rate.

The high intensity exponent obtained has also been explained by Bamford & Jenkins on the basis of this occlusion theory. The greater the initiator concentration, the greater will be the rate of production of polymer and hence the greater will be the elevation of the rate above that predicted by a square root dependence on initiator concentration. Extreme occlusion could also be regarded as a first order termination reaction but, in earlier papers, Bamford et al showed that the concentration of trapped radicals at 25°C was 1% (as estimated by reaction with DPPH[30]) of the total radical concentration and 2% of the total when estimated by a paramagnetic resonance technique[31]. The

most recent paper[32] quotes a value of 12.7 $\pm$ 3.5% for the fraction of radicals which become trapped at 17% conversion under the same conditions as for the above experiments. This figure was also obtained by an electron-spin resonance technique. It is claimed, therefore, that first order termination in this way has only a small effect on the value of the initiator exponent.

To summarise the occlusion theory due to Bamford et al, it may be said that the unusual polymerisation kinetics of acrylonitrile are explained by the lowering of the velocity coefficients of the constituent reactions due to the radical ends being occluded in polymer aggregates.

The above theory appeared to require a great deal more experimental testing. Although it was claimed that the velocity coefficients changed as the reaction progressed, no absolute values were obtained by the above workers. Also, the theory postulated that coalescence of the radical with a polymer aggregate had a greater effect on the velocity coefficients than the initial coiling of the radical in the non-solvent medium.

A comparison of the reported values for the propagation and termination coefficients for the bulk polymerisation of acrylonitrile and for the solution polymerisation disclosed interesting anomalies. These values are given in Table 1.

Table 1: Values reported for the velocity coefficients of propagation (k_2) and termination (k_4) in the bulk and solution polymerisations of acrylonitrile.

k_2	k_4	System	Temp. (°C)	Ref.
24	2.3×10^7	Bulk	50	22
127	1.2×10^7	Bulk	25	23
2,458	9.8×10^8	Solution	60	24

The two results quoted for bulk polymerisation are in reasonable agreement whereas, by the occlusion theory, a large difference in the values of k_4 would have been expected since the work of Durup & Magat[22] was carried out at a much higher percentage conversion than the work of Bengough[23]. Although there is an apparently large difference between the velocity coefficients for bulk and solution polymerisations, the reported values of the ratio of k_2/k_4 for these two systems do not vary by more than a factor of two [20, 22, 23, 24, 33].

The aim of this thesis has therefore been to investigate these polymerisations with a view to redetermining the velocity coefficients at the above concentrations and then to extend this

evaluation over the monomer concentration range from bulk polymerisation to polymerisation in dimethylformamide solution.

To do this, it was necessary to know the rate dependences on monomer and initiator concentration, and to have accurate values for the rate of initiation, the rate of reaction, and the corresponding kinetic chain lifetime. These have all been evaluated and, to minimise the effect of coalescence, non-stationary state methods have been used for the determination of rates of reaction and kinetic chain lifetimes.

Because of the difference between the published values for the energy of activation in the polymerisation of acrylonitrile (21.0 Kcal/mol. in solution[19] and 35.2 Kcal/mol. in bulk polymerisation[14], both found by using AIBN as initiator), the energy of activation has been determined over a wide range of monomer concentrations.

To complete Part I of this thesis, the transfer constants between acrylonitrile and dimethylformamide, and between acrylonitrile and bromotrichlormethane have been evaluated. The latter work was performed to afford comparison with results obtained in telomerisation studies.

In an attempt to separate the detailed discussion of experimental results from the general discussion as to their

significance with respect to the overall kinetic scheme, this thesis has been set out in chapter form. Each chapter deals with one topic or a closely related set of topics and it contains the theory of the methods under consideration, the experimental results, and the detailed discussion on these results.

The correlation of the individual results and the conclusions to be drawn from them are discussed in the final chapter of the first part of this thesis.

C H A P T E R 2.

EXPERIMENTAL

2.1. Materials:

2.1.1. Acrylonitrile (AN) :

The acrylonitrile (AN) (supplied by G.Light & Co.,) was dried over calcium chloride for 24 hours then filtered off and distilled at atmospheric pressure. Only the middle fraction, having a b.pt. of 77.3°C, was collected. This was stored over calcium chloride until required. After filtration, the redistilled acrylonitrile was poured into a round bottomed flask, some αα'-azo-bis-isobutyronitrile (AIBN) added and the flask connected up to the vacuum line. The AN - AIBN mixture

was thoroughly degassed before being photochemically polymerised to approximately 25% conversion. The required amount of pure acrylonitrile could then be distilled into the reaction vessel from this reservoir.

2.1.2. αα'-azo-bis-isobutyronitrile (AIBN) :

The Eastman Kodak technical grade of AIBN was purified by recrystallisation from absolute alcohol. The product had a m.pt. of 102°C accompanied by decomposition. Because of the small quantities of AIBN required for most of the polymerisations mentioned in this thesis, the initiator was normally used in chloroform solution. The maximum storage time of an AIBN - chloroform solution was two weeks, care being taken to shield it from any light source.

2.1.3. N,N-dimethylformamide (DMF) :

For all purposes, with the exception of experiments involving the use of ferric chloride, the DMF (as supplied by Eastman Kodak) was purified by careful fractional distillation, the fraction boiling at 153°C being collected.

2.1.4. αα'-diphenyl-β-picrylhydrazyl (DPPH) :

This was prepared by the method of Goldschmidt & Renn[34]. In this, the αα'-diphenyl-β-picrylhydrazine was prepared from unsym.-diphenyl-hydrazine hydrochloride, picryl chloride, and sodium bicarbonate. The hydrazine was then treated with anhydrous sodium sulphate and lead peroxide to give the αα'-diphenyl-β-picryl hydrazyl, the final recrystallisation being from ligroin and benzene mixture. This produced a 1:1 DPPH : benzene product[35] and the necessary corrections have been applied to the results obtained by using this inhibitor. For convenience, the DPPH was normally made up in chloroform solutions and these were frequently renewed to ensure reproducibility in the experimental results.

2.1.5. Bromotrichloromethane (BTCM) :

An Eastman - Kodak chemical, this was purified by washing with dilute sodium carbonate solution and then with water. The bromotrichloromethane was dried over calcium chloride and finally distilled under reduced pressure before use.

2.1.6. Solvents :

Analar grades of benzene, acetone, and chloroform were selected. These were all distilled before use.

2.2. Apparatus :

2.2.1. High Vacuum Line :

This consisted of a series of traps and vacuum tested taps in Pyrex glass connected to the pumping system of a Metrovac Oil Diffusion Pump backed by a Speedivac Rotary Oil Pump. The taps and joints were greased with Apiezon High Vacuum Greases suitable for the temperature conditions prevailing in the laboratory. Cold traps were placed immediately before and after the oil diffusion pump, liquid nitrogen being used as a coolant in the former to prevent contamination of the oil. A Drikold - acetone mixture was used as the coolant in the other cold trap and as the receiver coolant when distillation was taking place on the line.

No vacuum gauge was fitted to the system but the working pressure was roughly estimated by the discharge obtained from a high voltage coil (a Tesla coil) activated close to the vacuum line.

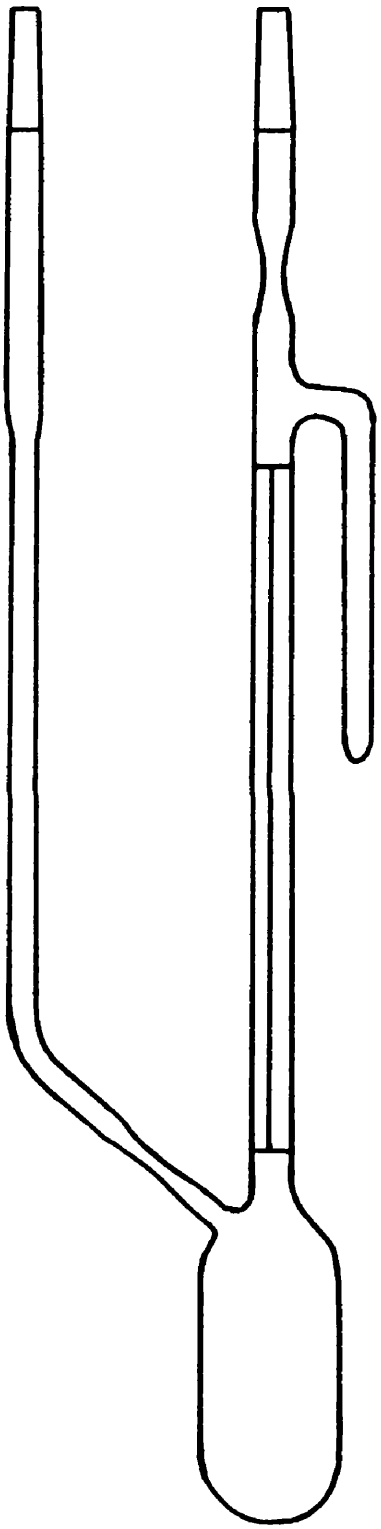


FIG. 1.

A pressure of about 10^{-4} mm. of mercury was easily attained, a pressure of 10^{-5} mm. of mercury being the rated performance of the pumping system.

2.2.2. Reaction Vessels :

All the reactions were carried out in Pyrex glass dilatometers. For thermal polymerisations, at temperatures above 50°C, dilatometers of approximately 2 ml. capacity were used. For most experiments, the reaction vessels were made from 1·5 cm. tubing to give a volume of around 20 ml. The dilatometer stems were of Veridia capillary tubing, the bore being chosen so that the rate of reaction could be conveniently measured.

For reactions involving measurements of the rate of reaction during the non-stationary state period, a special design of dilatometer was required (Fig.1). Since this had a stem of 0·4 mm. Veridia tubing, a wide bore side arm was necessary to allow the distillation of the reactants into the vessel to proceed at a reasonable rate. A reservoir was provided just above the level of the stem so that, by adjusting the volume of reactants, several accurate rate determinations could be

performed in each dilatometer.

When using the spectrophotometric method of evaluating the rates of initiation, the reaction tubes were carefully matched to give identical optical cross-sections. A locating collar on the tube ensured that this cross-section was reproducibly interposed between the light source and the photo-cell detector.

The determination of specific heats and coefficients of volume expansion of liquids was carried out in a dilatometer of 30 ml. volume and having a stem of 1.5 mm. Veridia. Two light metal washers in the bulb of the dilatometer moved through the liquid with a paddle motion when actuated by a magnet moving in a vertical plane outside the dilatometer bulb. Thus, efficient and reproducible stirring was obtained.

2.2.3. Thermostatically Controlled Tank :

All experiments were carried out under standard conditions in a cylindrical Pyrex glass tank. This was surrounded by an aluminium jacket having an observation and a irradiation window cut in the appropriate positions. The annular space between the tank and the jacket (about 1") was filled with fibreglass

lagging. The tank contained approximately 25 litres of water and a constant temperature ($\pm$ 0.02°C) was maintained by a relay operated filament heater, the relay circuit being actuated by a mercury - toluene detector. Efficient stirring was provided by a propeller stirrer.

2.2.4. Irradiation :

The source of irradiation was a 125 W. Osira high pressure mercury vapour lamp. To smooth out variations in the applied current, the lamp was connected to a capacitor and a choke. The emitted light was filtered through a Chance OX_1 filter.

2.2.5. Time Base :

An Elliot D.C. Pen Recording Voltmeter was used as a time base for the rate measurements in the non-stationary state experiments. A 1-volt dry cell battery was connected to the recorder and a resistance and a tapping key were so arranged that the circuit could be broken by depressing the key.

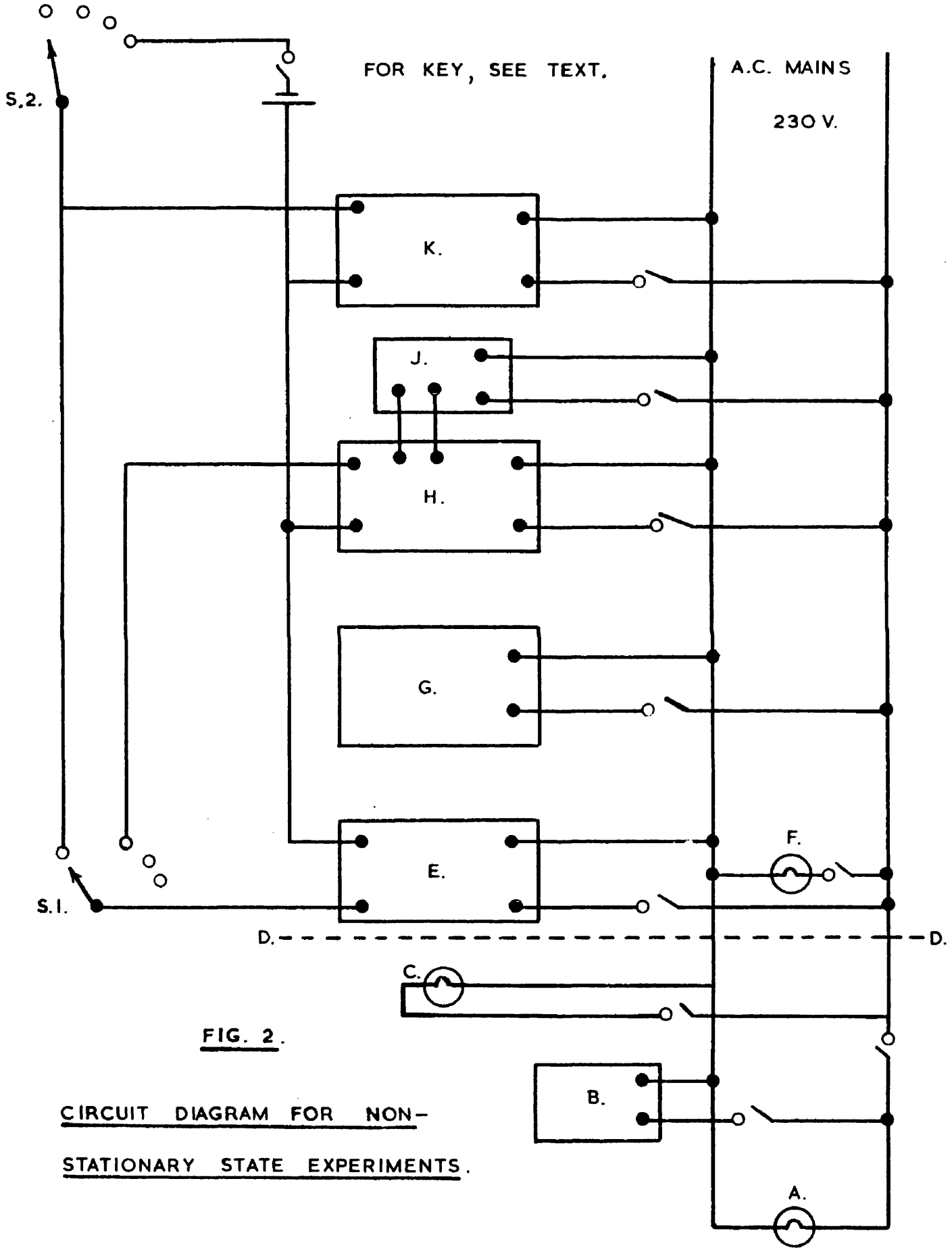


FIG. 2.

CIRCUIT DIAGRAM FOR NON-STATIONARY STATE EXPERIMENTS.

2.2.6. Rotating Sector and Non-Stationary State :

Fig.2 shows the circuit for the modified rotating sector and non-stationary state experiments. The key to the figure is given below.

A - Viewing lamp in thermostat.

B - Shutter solenoid.

C - Excitation lamp for photo-cell.

D - Plane of sector.

E - Photo-electric cell.

F - Mercury vapour lamp.

G - Variable speed electric motor.

H - Cathode-ray oscilloscope.

J - Elliot D.C. Pen-recording Voltmeter

S_1 - Two bank switch.

S_2 - Two bank switch.

A light aluminium disc about 14 ins. in diameter was divided into four sectors. Two of the sectors were cut out so that equal light and dark periods were obtained. (This disc will now be referred to simply as "the sector"). The sector was driven by a variable speed motor through a 25:1 reduction

gear. For the measurement of long flash times, the output of the photocell was fed into the Elliot pen recorder whilst for short flash times, the output of the photocell was matched against the standard output of a signal generator by means of an oscillograph.

2.3. Procedure :

Since it has been shown that oxygen inhibits acrylonitrile polymerisation,[36,37] all reactions were carried out under vacuum.

2.3.1. Calibration of dilatometers :

The dilatometers were thoroughly cleaned and the volume of the bulbs found by using A.R. acetone. The volume of the capillary stem was checked by weighing the quantity of mercury which occupied a known length of the stem. Since the densities of the final products were known, the rate of fall of the meniscus in the dilatometer stem could be directly correlated to the rate of reaction.

2.3.2. Filling of dilatometers :

Initiators and inhibitors were introduced into the reaction vessel in standard chloroform solutions. The dilatometer was connected to the vacuum line and the solvent distilled off. If the other reactants were volatile (e.g. acrylonitrile), they were distilled directly into the dilatometer and this was then sealed off at the constriction.

If, however, one of the reactants did not distil readily on the vacuum line, another technique was used. After the solvent had been distilled from the initiator and/or the inhibitor solution, the dilatometer was disconnected from the vacuum line and the non-volatile reactant measured in. The dilatometer was reconnected to the vacuum line and immersed in a Drikold-acetone mixture before opening the tap which was isolating the dilatometer from the high vacuum system. The air in the reaction vessel was pumped off over a period of 30 mins. and then the isolating vacuum tap was closed. The reactants were heated to 25°C then immersed again in the Drikold-acetone coolant before opening the isolating tap. This freezing - evacuating - thawing cycle was repeated three times and will be referred to simply as degassing. Any other volatile reactants were then distilled

in as described above.

Since DMF distilled very slowly at low pressures, the above degassing process was used for all reaction mixtures containing DMF.

When the dilatometer stem was of 0.4 mm. capillary, a further modification had to be introduced. In this, degassing and distillation were effected through a wide - bore side arm to increase the rate of both processes. (Fig.1).

If the reaction mixtures were not to be used immediately, they were stored in darkness in a Drikold-acetone coolant until required.

2.3.3. Rate measurement :

The filled dilatometers were completely immersed in the thermostat at the required temperature. For photoinitiated polymerisations, the reaction vessels were left in the thermostat for 20 minutes to come to thermal equilibrium with its surroundings before irradiation began. In thermal polymerisations, readings were taken 2 minutes after placing the dilatometer in the tank. By using narrow dilatometers, it was found that thermal equilibrium was attained in less than 3 minutes.

The rate of reaction of the polymerisations was measured

dilatometrically by following the rate of fall of the meniscus level in the dilatometer stem using a cathetometer. This was readily converted to an absolute value for the rate of reaction.

2.3.4. Physical Constants required for non-stationary state work :

(a) Density :

This was found by weighing a standard volume of the liquid in a pyknometer and comparing it with the weight of an equal volume of a liquid of known density.

(b) Coefficient of Expansion :

The dilatometer described in section 2.2.2. was placed in a thermostat at 25°C and the corresponding changes in volume were noted. Efficient stirring ensured that thermal equilibrium was quickly attained.

(c) Specific Heat :

The dilatometer used in (b) above was heated to about 32°C and then placed in an air jacket in the 25°C thermostat. The rate of fall of the meniscus was measured and equated to the rate of cooling. The specific heat of the liquid was found

by comparing its rate of cooling with that of a liquid of known specific heat. Application of Newton's Laws of Cooling to this system was entirely justified since both the rate of stirring of the mixture and the surrounding thermal conditions were reproducible.

2.3.5. Rate Dependence on Initiator Concentration :

This was carried out at 60°C for the bulk polymerisation of acrylonitrile using AIBN concentrations varying from 4.38×10^{-5} mol./l. to 3.80×10^{-3} mol./l.

For solution polymerisation the reaction was photoinitiated at 25°C using AIBN concentrations varying from 3.80×10^{-3} mol./l. to 5.0×10^{-4} mol./l. An 80% DMF - 20% acrylonitrile (v/v) reaction mixture was used.

2.3.6. Rate Dependence on Monomer Concentration :

A series of photoinitiated polymerisations was carried out at 25°C using reaction mixtures containing varying proportions of DMF and acrylonitrile. The concentration of AIBN was held constant at 3.80×10^{-3} mol./l. and the reaction mixtures varied from 10% DMF - 90% acrylonitrile (v/v) to 90% DMF - 10% acrylonitrile (v/v).

2.3.7. Intensity Exponents :

The intensity exponent was determined by inserting a wire gauze screen of known transmission in the path of the initiating irradiation. The rate of the reaction at full intensity was compared to the rate at this reduced intensity. After removing the screen, the rate at full intensity was again measured to ensure that this was a constant over the duration of the experiment. To obtain an approximate value of the intensity exponent for heterogeneous polymerisations, the rate at full intensity was taken as the average of the two values obtained.

2.3.8. Heat of Polymerisation :

This was found using the dilatometric method of Bengough[38] and was required for the conversion of initial expansion rates to absolute reaction rates.

The dilatometer containing the reactants was allowed to come to equilibrium in the thermostat and then the level of the meniscus in the stem was adjusted by using the excess reactants in the dilatometer reservoir (Fig.1 and 2.2.2.). After equilibrium had again been attained, the shutter was

removed and the dilatometer irradiated. The rate of rise of the meniscus was followed using the tapping key linked to the Elliot Pen Recorder. A 100 division graticule in the eyepiece of the cathetometer allowed this expansion to be easily measured. A trace giving peaks corresponding to each graticule division was obtained and, from the graticule calibration and the speed of the chart, the expansion rate was calculated. More reactants were then added from the dilatometer reservoir until the meniscus level was above the top of the stem. The dilatometer was irradiated for about 15 minutes and a measurement of the steady rate was taken as the meniscus travelled down the stem. The shutter was replaced in the path of the light and the contraction due to cooling measured. This sequence of experiments was repeated four times allowing a 20 minute time interval between each one to ensure steady conditions.

For some experiments, the dilatometer was placed in a vacuum jacket which was then immersed in the thermostat. This lengthened the period of adiabatic conditions in the reaction system.

The heat of reaction was measured for the polymerisation of acrylonitrile in bulk, and in DMF solution.

2.3.9. Measurement of Radical Lifetime.

Two methods were used, one being the dilatometric method[39] and the other being a combination of this method with the rotating sector method.[40-44] Both methods gave the lifetime of the growing chain in the very early stages of the reaction.

(a) Dilatometric Method :

The initial expansion, measured as in 2.3.8., was plotted against time. The linear portion of this curve was projected back to meet the time axis and the value of τ , the radical lifetime, was calculated. This method was used for heterogeneous polymerisations where the lifetime was greater than 0.5secs.

(b) Modified Rotating Sector Technique[45]:

The apparatus used for the measurement of the flash time is described in 2.2.6. and the dilatometer used is shown in Fig.1. The dilatometer was filled as described in 2.3.2. and allowed to come to thermal equilibrium in the thermostat at 25°C. The initial expansion rate was measured at full light intensity and then at various flash times. The flash time was measured before and after the measurement of the initial expansion rate and the mean flash time was taken to correspond to the expansion rate. The ratio of the sectored rate to the

rate at full intensity was then plotted against log.(flash time). By matching this graph with the theoretical one, a value for the lifetime, τ , was obtained.

This method was used for lifetimes of less than 0.5 secs.

2.3.10. Rate of initiation:

This was estimated using DPPH as an inhibitor or as a radical scavenger. The rate of removal of the DPPH was measured spectrophotometrically at 5,240 Å in three solvents - acrylonitrile, chloroform, and benzene. The rate of removal of DPPH was also found by direct measurement of the inhibition period produced by the DPPH in the bulk polymerisation of acrylonitrile.

For ideal inhibitor kinetics, the absolute rate of removal of the inhibitor must be independent of the concentration of inhibitor for any given initiator concentration i.e. the time taken to remove the inhibitor must be directly proportional to the concentration of inhibitor. A radical scavenger should also show these kinetic characteristics. Thus, a series of experiments was carried out in each solvent in which the AIBN concentration was held constant and the DPPH concentration varied.

Using a constant DPPH concentration, a second series of experiments was performed to find the relationship between rate of removal of DPPH and the AIBN concentration.

In all the spectrophotometric experiments, the initial concentration of DPPH in a reaction mixture was checked from a calibration curve relating optical density to DPPH concentration. A blank experiment on a reaction mixture containing only DPPH and solvent was carried out in all three solvents.

As a result of a paper published by Bamford & Jenkins[46], using ferric chloride as a retarder, an attempt was made to apply this method to photochemical polymerisations.

2.3.11. Isolation of Reaction Products :

The polymers produced in the reactions were disolved in a large excess of DMF and precipitated by pouring this dilute solution into a volume of methanol which was 10 times greater than the volume of the DMF solution. Vigorous stirring accompanied this precipitation and the polymer was obtained in a finely divided form. The polymer was then filtered off washed with methanol and dried at 60°C.

2.3.12. Determination of Molecular Weights :

About 0,2 g. of the dried polymer was weighed and dissolved in 25 ml of DMF. The mol. wt. was determined viscometrically using an Ubbelohde viscometer modified so that the polymer solution could be diluted and stirred *in situ*. The time of flow of polymer solutions of various concentrations was found and, knowing the time of flow of the DMF solvent, the specific viscosity was readily obtained. The intrinsic viscosity was found by applying the Schulz - Sing relationship[47] to the observed specific viscosity.

2.3.13. Determination of transfer constants :

For this, the degree of polymerisation of the products of reactions involving various molar ratios of transfer agent to monomer was found as in 2.3.11. and 2.3.12. Using the theory suggested by Mayo[48], the value of the velocity coefficient for transfer was found.

CHAPTER 3.

Physical Constants.

In this chapter, values for the physical constants required for the later kinetic analyses are given. Where well substantiated figures were available in the literature, these were used in the present work and the relevant references are quoted in the following sections.

3.1. Theory of the calculation of specific heats.

The determination of the specific heats was carried out using a refined application of Newton's Cooling Curves[49]. In this, it is assumed that, for any given volume having a

stated surface area, the rate of cooling at any given temperature is proportional to the reciprocal of the heat capacity of the material.

Therefore, if the rate of cooling of a liquid is compared to the rate of cooling of a liquid of known specific heat under identical conditions, the specific heat of the former liquid can easily be found from the following equation.

$$dT_a/dt \cdot (W_a S_a + E) = dT_b/dt \cdot (W_b S_b + E) \quad \ldots(3.1)$$

where W and S are the weight and specific heat of the liquid, dT/dt is the rate of cooling, and E is the water equivalent of the containing vessel. The subscripts a and b denote the two liquids under consideration. In the present determination, identical conditions were ensured by having reproducibly constant stirring (see section 2.2.2.) and by taking the rate of cooling at an accurately defined temperature.

3.2. Results.

3.2.1. Coefficient of volume expansion:

The expansion - temperature curves are shown in Fig. 3, the expansion being given in arbitrary units (in this case,

FIG. 3

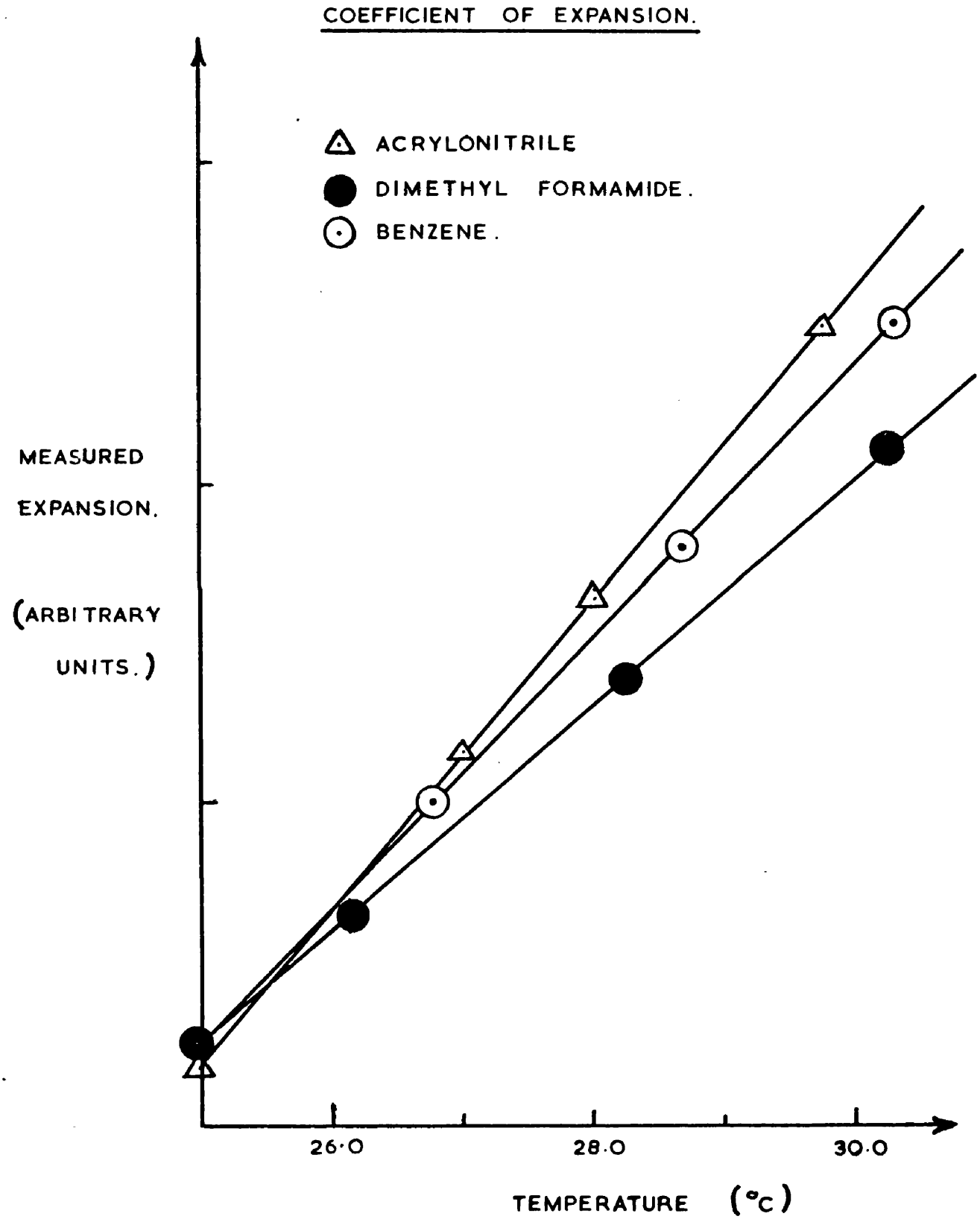
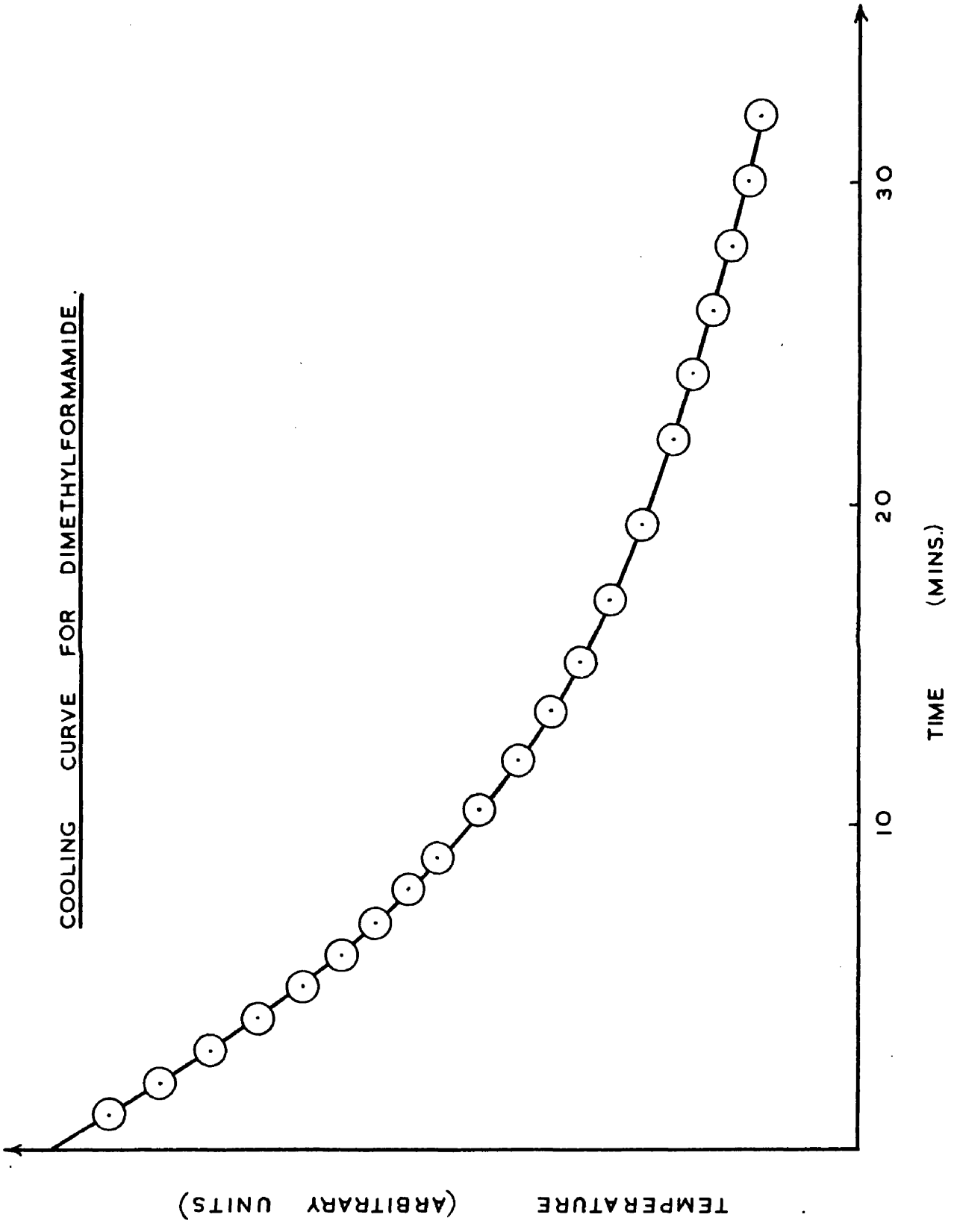

COEFFICIENT OF EXPANSION.
ACRYLONITRILE
DIMETHYL FORMAMIDE.
BENZENE.
MEASURED
EXPANSION.
(ARBITRARY
UNITS.)
26·0
28·0
30·0
TEMPERATURE (°C)

FIG. 4

COOLING CURVE FOR DIMETHYLFORMAMIDE.



cm. of the stem of the dilatometer) which could be directly correlated to the absolute expansion. The experimental results obtained are given in Table 2.

Table 2. Values of the Coefficient of Volume Expansion

Material	Coefficient.
Acrylonitrile	1.405×10^{-3}
Dimethylformamide	1.029×10^{-3}
Benzene	1.230×10^{-3}
Carbon tetrachloride	1.235×10^{-3}
80% DMF - 20% AN mixture $(\frac{v}{v})$	1.069×10^{-3}

3.2.2. Specific heat of reactants.

The two reference liquids used to determine the required specific heats were carbon tetrachloride and benzene. The sp. hts. of these substances are 0.201^{50} and 0.414^{50} cal/g. respectively. A typical cooling curve is shown in Fig. 4 and the results obtained are given below.

Table 3. Specific heats of the reactants.

Material	Mean sp. ht. (cals/g.)
Acrylonitrile	0.45
Dimethylformamide	0.60
80% DMF - 20% AN mixture	0.56

Using the experimentally determined values for the sp. hts. of acrylonitrile and DMF, the calculated composite sp. ht. of an 80% DMF - 20% AN mixture (v/v) was found to be 0.57, which agrees fairly well with the experimental determination for this mixture.

3.2.3. Density of reagents :

The densities of the reagents used in this thesis are given in Table 4. These were mainly obtained from published literature.

Table 4. Densities of reagents.

Material	Density$_{25^oC}$ (g./ml.)	Ref.
Acrylonitrile	0.8004	51
DMF	0.948	Present Work

Table 4. continued

Material	Density $_{25^{o}C}$ (g./ml)	Ref.
DMF	0.944	52
Acetone	0.7844	53
Carbon tetrachloride	1.592	53
Benzene	0.877	53
Polyacrylonitrile	1.19	20

3.2.4. Absolute monomer concentration in the various reaction mixtures.

The reaction mixtures used in this thesis are frequently described by their percentage composition by volume. When this is done, the absolute monomer concentration is not easily appreciated and thus, Table 5 has been constructed.

Table 5. Equivalence of absolute monomer concentration and percentage volume composition (at 25°C) of reaction mixtures containing acrylonitrile and DMF

System	Monomer Concentration. (mol./l.)
Bulk acrylonitrile	15.10

Table 5. Continued.

System.	Monomer Concentration. (mol/l.)
5% DMF - 95% AN	14.31
10% DMF - 90% AN	13.55
20% DMF - 80% AN	12.05
30% DMF - 70% AN	10.54
40% DMF - 60% AN	9.05
50% DMF - 50% AN	7.54
60% DMF - 40% AN	6.03
70% DMF - 30% AN	4.54
80% DMF - 20% AN	3.02
90% DMF - 10% AN	1.51

3.3. Discussion.

3.3.1. Coefficient of Expansion.

The values quoted in Table 2 for benzene and carbon tetrachloride are in excellent agreement with the literature figures[54]. Thus, it may be assumed that the other results obtained using this method are also accurate. The agreement between the experimental and the calculated composite coefficient

of expansion for an 80% DMF - 20% AN mixture was also good and the value used in future calculations is the mean of these, 1.087×10^{-3}.

3.3.2. Specific heats.

The agreement between the experimental and the calculated composite specific heat for an 80% DMF - 20% AN mixture was very good, the value of 0.57 being used for future work.

CHAPTER 4

Heat of Polymerisation.

In order to evaluate the absolute rate of polymerisation from data obtained in the non-stationary state and rotating sector methods (Chapter 7), it is necessary to know the value of the heat of polymerisation.

4.1. Theory of the dilatometric method of determining the heat of polymerisation[38].

The normal techniques for determining the heat of reaction involve adiabatic or isothermal calorimetry.[55-58] These methods either measure the heat evolved for a known percentage reaction

or the rate of evolution of heat together with the rate of reaction. The method used in the present work involves the measurement of the rate of reaction during the thermally steady state i.e. when the rate of self heating of the reaction mixture is equal to the rate of loss of heat to its surroundings. The latter quantity can be easily measured by stopping the reaction suddenly and following the subsequent rate of cooling. The value of the initial expansion rate obtained on commencement of irradiation, together with the value of the steady rate, can also be used to evaluate the heat of polymerisation.[59,60]

Three different effects, each producing a change of volume, act simultaneously during the polymerisation of acrylonitrile. The self-heating due to polymerisation tends to produce an increase in volume whilst the difference between the density of the reactants and the final products produces a contraction. The heat loss from the reaction mixture to its surroundings will also cause a contraction. Thus, at any time during the polymerisation, the overall rate of contraction, C, is given by:

$$C = Z + Y - \varepsilon \qquad \ldots(4.1.1)$$

where Z is the rate of contraction due to reaction, Y is the

rate of contraction due to the heat loss to the surroundings, and ε is the rate of expansion due to self-heating in the reaction mixture.

If the polymerisation proceeds at X%/sec., then

$$Z = X.(\rho' - \rho)/\rho' \qquad \ldots(4.1.2)$$

where ρ and ρ' are the densities of the monomer and polymer respectively and

$$\varepsilon = X.\Delta H.\alpha/S.m \qquad \ldots(4.1.3)$$

where ΔH is the heat of polymerisation (cal/mol), α is the coefficient of expansion, and S and m are the specific heat and molecular weight of the monomer respectively.

From (4.1.2) and (4.1.3) we get:

$$\Delta H = \varepsilon.S.m(\rho' - \rho)/Z.\alpha.\rho' \qquad \ldots(4.1.4)$$

Since all the physical constants are easily obtained (Chapter 3), the value of ΔH may be evaluated by measuring the ratio of ε/Z.

The rate of contraction due to reaction, Z, can be measured when the system attains a steady thermal state. From equation (4.1.1), Z must then equal C, the overall rate

of contraction.

The value of Y, the rate of contraction due to cooling, may be obtained by measuring the initial rate of cooling on cessation of irradiation. At the steady thermal state, this will be numerically equal to ξ .

Alternatively, the value of ξ may be found during the first 10 to 15 secs. of the reaction when the reaction vessel may be considered as an adiabatic system. In this case, Y = 0 so that C = Z - ξ . For the polymerisation of acrylonitrile, $\xi > Z$ i.e. an expansion occurs during the adiabatic period. The rate of expansion due to self-heating is therefore equal to the sum of the measured initial expansion rate and the steady rate of contraction due to reaction.

The above discussion has been applied simply to the bulk polymerisation of a monomer. For systems containing more than one component, composite values of the physical constants (see sections 3.2.1 and 3.2.2.) are used in equation (4.1.4). These composite values must all be based on reaction mixtures containing 1 mol. of the monomer. Thus, the product of S x m in equation (4.1.4) becomes the heat capacity of the reaction mixture which contains 1 mol. of monomer.

4.2. Results.

4.2.1. Conversion factors required for the dilatometric determination of the heat of polymerisation.

Equation (4.1.4) may be written:

$$\Delta H = K.\ \varepsilon/Z \qquad \ldots(4.2.1)$$

where

$$K = S.m\ (\rho' - \rho)/\alpha.\rho' \qquad \ldots(4.2.2)$$

Table 6 gives the values of K required for the evaluation of the heat of polymerisation of acrylonitrile in bulk and in DMF solution.

Table 6. Conversion factor required for the dilatometric determination of the heat of polymerisation at 25°C.

System	K
Bulk acrylonitrile	5.59
80% DMF - 20% AN mixture	10.51

4.2.2. Bulk polymerisation.

The results obtained for the heat of polymerisation in the

bulk polymerisation of acrylonitrile at 25°C are given in Table 7.

Table 7. Heat of Polymerisation in the bulk polymerisation of acrylonitrile.

Steady Rate*	Init.Expn. Rate*	Cooling Rate*	ΔH Kcal./mol.
2.47	4.97	-	16.8
3.30	-	7.59	12.8
3.29	-	7.16	12.1
2.47	-	7.16	16.2
3.30	4.54	-	13.2
3.29	3.25	-	11.1

* Rates expressed in arbitrary units.

This gives an average value of 13.7 Kcal./mol. for the heat of reaction in the bulk polymerisation of acrylonitrile.

4.2.3. Solution polymerisation :

The following results for the heat of polymerisation were obtained in a reaction mixture containing 80% DMF and 20% acrylonitrile by volume. A typical determination is shown

FIG. 5

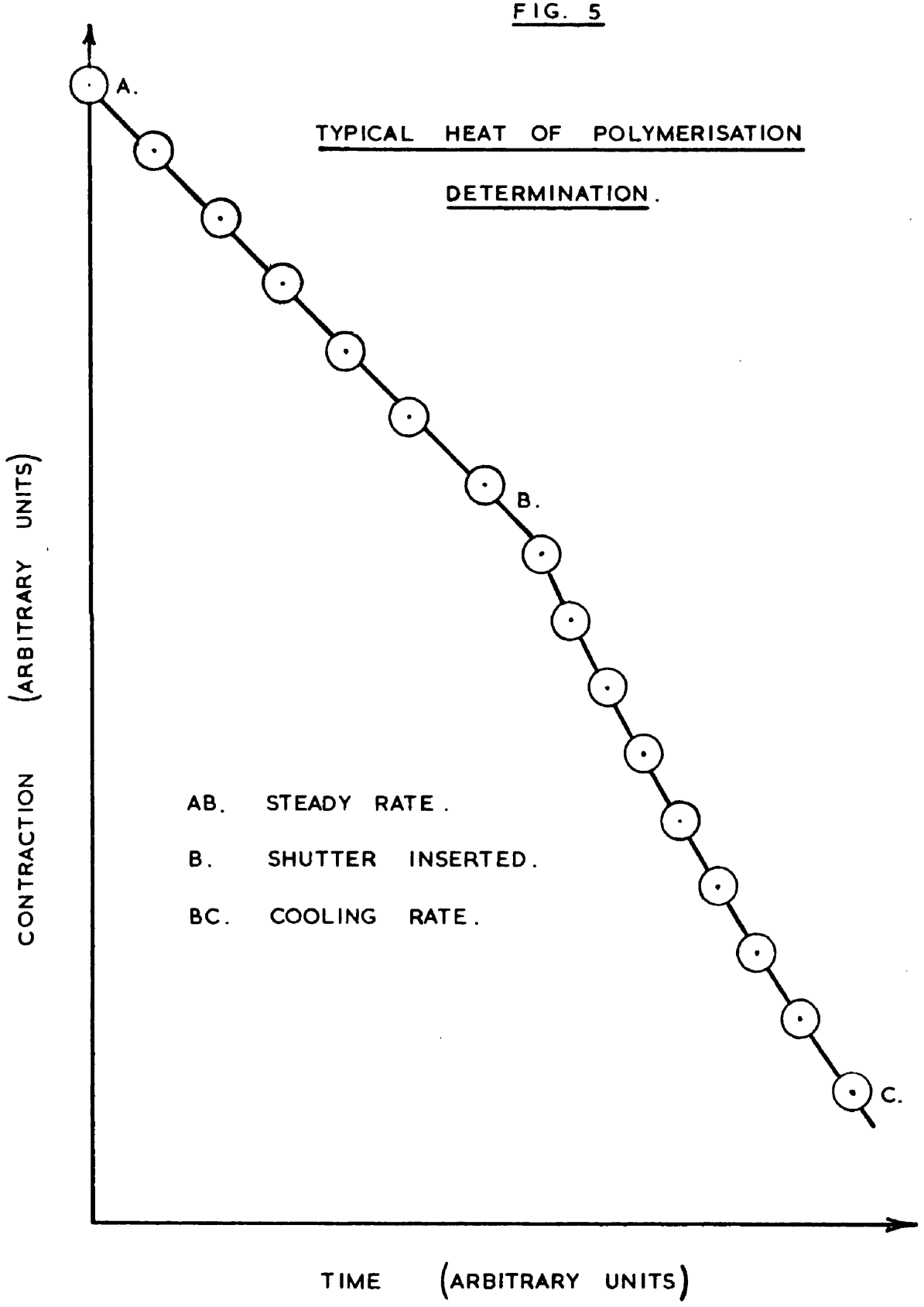
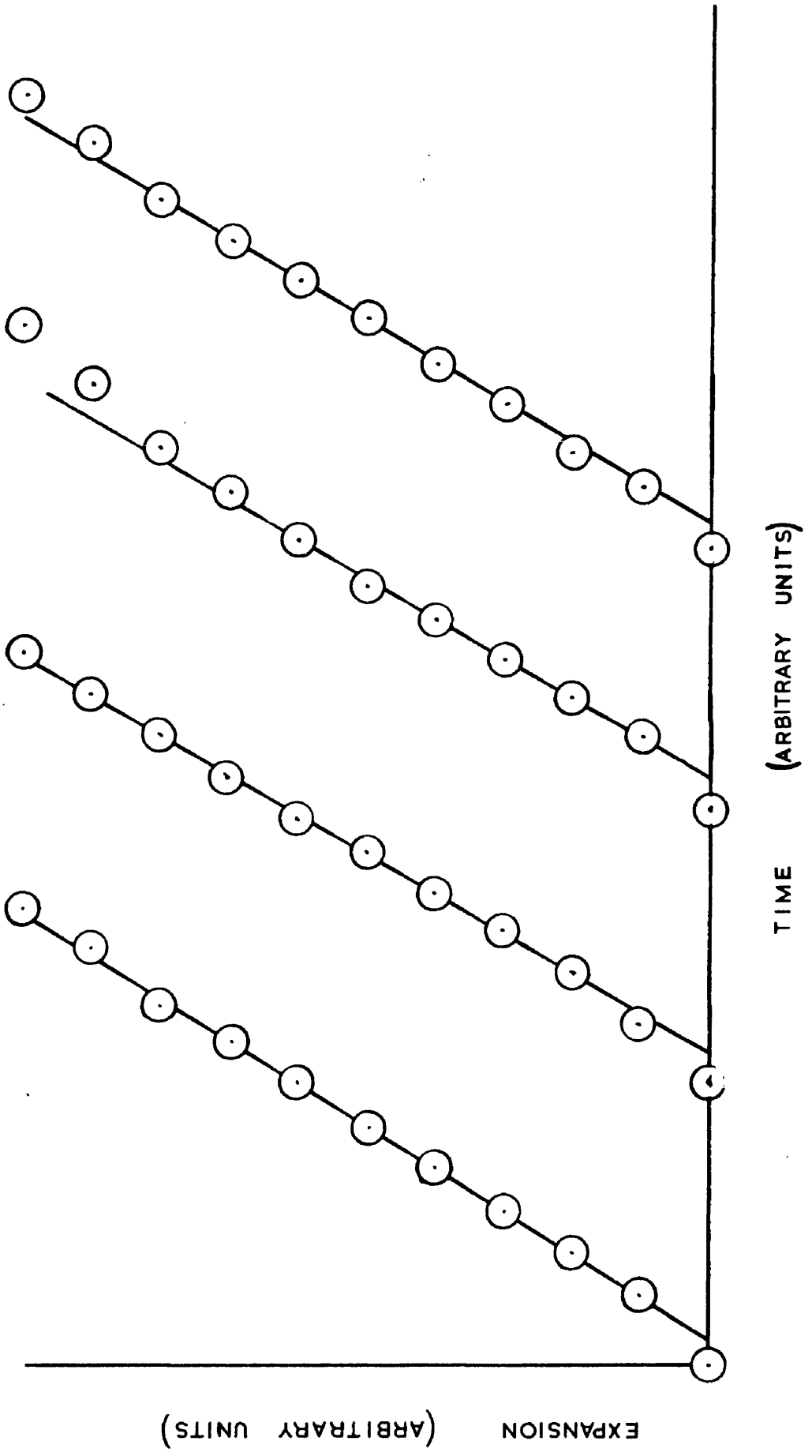

TYPICAL HEAT OF POLYMERISATION
DETERMINATION.
A.
B.
C.
AB. STEADY RATE.
B. SHUTTER INSERTED.
BC. COOLING RATE.
CONTRACTION (ARBITRARY UNITS)
TIME (ARBITRARY UNITS)

FIG. 6

TYPICAL INITIAL EXPANSION CURVES OBTAINED BY THE DILATOMETRIC METHOD.



in Fig. 5 whilst a series of initial expansion curves are shown in Fig. 6.

Table 8. Heat of polymerisation of acrylonitrile in solution polymerisation.

Steady Rate*	Init.Expn. Rate*	Cooling Rate*	ΔH (Kcal/mol.)
0.45	-	0.99	23.2
0.45	0.50	-	22.2
0.27	-	0.54	21.5
0.39	-	0.88	23.9
1.03	1.04	-	21.1
1.03	-	2.05	21.1
1.03	-	2.44	24.8
1.03	-	2.38	24.2
2.17	-	2.17	20.6**
2.63	-	4.27	23.9**
1.01	-	2.57	26.6**
1.01	1.39	-	24.9**
1.14	-	2.25	20.8
0.48	-	1.07	23.5
1.61	-	2.06	21.4

Table 8 Continued

Steady Rate*	Init.Expn. Rate*	Cooling Rate*	ΔH (Kcal./mol.)
1.31	1.40	-	23.5
1.31	-	2.79	23.6

* Rates expressed in arbitrary units.

** Experiment performed with dilatometer in a vacuum jacket.

This gives an average value of 23.0 Kcal./mol. for the heat of polymerisation of acrylonitrile in solution.

4.3. Discussion.

The results obtained in both systems for the heat of polymerisation show a far greater scatter than is normally obtained by this method.

The average value of ΔH for solution polymerisation is much higher than the value of 17.5 $\pm$ 0.5 Kcal./mol. reported by Tong & Kenyon[61]. No explanation can be given at present for this discrepancy.

The average value found for ΔH in the bulk polymerisation of acrylonitrile is much lower than the Tong & Kenyon value quoted

above. This may be due in part to the time taken to reach the steady rate being greater than the period in which adiabatic conditions exist in the dilatometer.

Because of these largely unexplained discrepancies in the experimental results, a heat of polymerisation of 17.5 Kcal./mol.[61] has been used in the following calculations.

4.4. Calculation of the absolute reaction rate from the measured initial expansion rate.

$$\left.\begin{array}{l}\text{Fractional expansion due to}\\ \text{heating for complete reaction}\\ \text{(adiabatic conditions)}\end{array}\right\} = \frac{\Delta H.\alpha}{C} \qquad \ldots(4.4.1)$$

$$\left.\begin{array}{l}\text{Fractional contraction for}\\ \text{complete reaction}\end{array}\right\} = \frac{V - V'}{V} \qquad \ldots(4.4.2)$$

where V is the initial volume of the reaction mixture which contains one mol. of acrylonitrile and V' is the final volume of the mixture after 100% conversion of monomer to polymer has occurred.

If adiabatic conditions were maintained over the duration of the reaction, then :

$$\left.\begin{array}{l}\text{Theoretical measured expansion} \\ \text{for complete reaction}\end{array}\right\} = \frac{\Delta H.\alpha}{C} - \frac{V - V'}{V}$$

$$= \Psi_o \qquad \ldots(4.4.3)$$

where C is the heat capacity of the reaction mixture which contains 1 mol. of monomer.

Since both quantities on the right hand side of equation (4.4.3) will vary in direct proportion to the percentage of reaction which occurs, at any stage of the reaction we may write:

$$\text{Theor. measured expn./sec.} = \frac{\Delta H.\alpha}{C} \cdot \frac{X}{100} - \frac{V - V'}{V} \cdot \frac{X}{100} \qquad \ldots(4.4.4)$$

where X is the percentage conversion/sec.

If, therefore, F_t is the measured fractional expansion/sec. in the initial stages of the reaction when the system is adiabatic, and if [M] is the monomer concentration in mol./l., then:

$$\text{Rate of reaction} = [M]\, F_t / \Psi_o \ \text{mol.l.}^{-1}\text{sec.}^{-1} \qquad \ldots(4.4.5)$$

Table 9 shows the value of Ψ_o for various reaction systems.

Table 9. Values of the theoretical measured expansion for complete reaction required for the conversion of initial expansion rates to absolute reaction rates.

System	Ψ_o
Bulk acrylonitrile	7.02×10^{-1}
5% DMF - 95% AN	6.23×10^{-1}
20% DMF - 80% AN	4.36×10^{-1}
40% DMF - 60% AN	2.49×10^{-1}
60% DMF - 40% AN	1.24×10^{-1}
70% DMF - 30% AN	7.59×10^{-2}
80% DMF - 20% AN	4.36×10^{-2}

The data in Table 9 has been calculated for reactions at 25°C.

A typical evaluation of the absolute reaction rate from the measured initial expansion rate is given below. The results were obtained from a modified sector experiment using an 80% DMF - 20% AN reaction mixture.

Volume of dilatometer = 21.20 ml.

Vol. of 1 cm. of dil. stem = 1.259×10^{-3} ml.

100 graticule divisions = 2.510 cm of dil. stem.

$\therefore$ 1 graticule division $= 3.158 \times 10^{-5}$ ml.

i.e. Fractional expn. equivalent to 1 graticule division $= 1.49 \times 10^{-6}$

Measured init. expn. rate $= 0.477$ grat.divs./sec.

$\therefore$ Measured fr. expansion/sec. $= 7.11 \times 10^{-7}$

Concentration of monomer $= 3.02$ mol./l.

$\therefore$ Rate of reaction $= \dfrac{7.11 \times 10^{-7}}{4.36 \times 10^{-2}} \cdot 3.02$

i.e. $\underline{\text{Rate of reaction}} = \underline{4.92 \times 10^{-5} \text{ mol.l.}^{-1} \text{ sec.}^{-1}}$

C H A P T E R 5.

Rate dependences, intensity exponents, and rate - time relationships for the polymerisation of acrylonitrile.

The complete kinetic scheme for a polymerisation reaction is extremely complex and it would be difficult to relate it to experimental results. The following simplifying assumptions are therefore made.

(a) Transfer to monomer is negligible.

The values reported for the ratio of k_m/k_2 [62-64] in acrylonitrile polymerisation are all around 2.0×10^{-5}. Since k_m is the velocity coefficient for the monomer transfer reaction,

it can be seen that this reaction is of no great importance to the overall kinetic scheme.

(b) The reactivity of the growing chain is independent of the chain length.

The reactive radical intermediates in vinyl polymerisations are all of a similar type, containing varying numbers of the same structural unit. The kinetic treatment must consider radicals of all sizes and it is generally assumed that the reactivity of any given type of radical is independent of its chain length. Thus, one velocity coefficient can be used for all the propagation steps occurring in the polymerisation of the monomer. Similarly, a single velocity coefficient can characterise all the termination steps or all the transfer reactions between the growing radical and any other single reactant. This assumption leads to kinetic equations which agree with the majority of the results so far obtained for vinyl polymerisations. Attempts have been made to test this assumption in other ways[65-67] but no conclusive results have been forthcoming.

(c) Evaluation of the rate of polymerisation.

The rate of polymerisation is generally taken to be equal to the rate of removal of monomer in the propagation step, neglecting any consumption of monomer in initiation or transfer

reactions as this will be negligibly small where high polymer is produced.

(d) Termination between primary radicals.

This step is not normally shown in the kinetic scheme since a factor allowing for this - the initiator efficiently - is generally applied to the experimental value of the rate of initiation.

(e) Stationary state.

The final approximation is to assume a stationary state condition[68] i.e. the concentration of the reactive radical intermediates remains constant during the reaction. This approximation obviously does not apply to the very early stages of the reaction and can only be applied to the polymerisation when the concentration of the reactants remains virtually constant.

The change over from the non-stationary to the stationary state is considered in more detail in chapter 7.

5.1. Kinetic scheme for vinyl polymerisation.

The following kinetic scheme, based on the above assumptions, is now generally accepted.

	Rate	
$C \rightarrow 2C\cdot$ $C\cdot + M \rightarrow R_1$	I	...(5.1.1) ...(5.1.2)
$R_1 + M \rightarrow R_2$ $R_n + M \rightarrow R_{n+1}$	$k_2[R][M]$	...(5.1.3)
$R_r + X \rightarrow P_r$	$k_5[R][X]$	...(5.1.4)
$R_r + R_s \rightarrow P_r + P_s$ $R_r + R_s \rightarrow P_{r+s}$	$k_4[R_r][R_s]$	...(5.1.5)

where C and M are molecules of initiator and monomer respectively, C· is a radical derived from the initiator, R is a growing radical, P is a molecule of dead polymer, and k_2, k_4, and k_5 are the velocity coefficients for propagation, second order termination, and first order termination respectively. The subscripts refer to the number of monomer units in the chain.

5.1.1. Second order termination.

In this case, termination will be as described in equation (5.1.5) i.e. either by combination or by disproportionation.

By assuming stationary state conditions:

$$d[R]/dt = I - k_4[R]^2 = 0 \qquad \ldots(5.1.6)$$

and if $[R_s]$ is the concentration of radicals during this period

$$[R_s] = (I/k_4)^{\frac{1}{2}} \qquad \ldots(5.1.7)$$

The rate of reaction will therefore be given by:

$$-d[M]/dt = k_2[R_s][M]$$

$$= k_2 \cdot \frac{I^{0.5}[M]}{k_4^{0.5}} \qquad \ldots(5.1.8)$$

5.1.2. First order termination.

Termination in this case is by step (5.1.4). Again assuming stationary state conditions,

$$d[R]/dt = I - k_5[R_s][X] = 0 \qquad \ldots(5.1.9)$$

where X is a molecule of an electron accepting compound.

i.e. $$R_s = I/k_5[X] \qquad \ldots(5.1.10)$$

The rate of reaction in this case will therefore be given by:

$$-\frac{d[M]}{dt} = \frac{k_2}{k_5} \cdot \frac{I \cdot [M]}{[X]} \qquad \ldots(5.1.11)$$

5.2. Rate - time relationships.

From the kinetic schemes described above, the rate of reaction should be a constant when the reactants can be taken as having virtually constant concentrations. At later stages of the reaction, the rate should decrease due mainly to the depletion of the monomer concentration. By plotting the rate of reaction against time, it should be possible to show whether or not the above kinetic schemes can be applied to the polymerisation of acrylonitrile.

5.3. Rate dependences.

By experimentally deriving the relationships between the rate of reaction and the concentrations of monomer and initiator and comparing these with equations (5.1.8) and (5.1.11), the kinetic order of the termination step may be found.

Similar information may be obtained by evaluating the rate dependence on the intensity of the initiating irradiation. The value found is normally called the intensity exponent.

5.3.1. Evaluation of intensity exponents.

Let the rate of reaction at full intensity be w_f.

Let the rate of r. at reduced intensity be w_r.

Let the intensity exponent be x, then for any given system:

$$\frac{w_f}{w_r} = \frac{\{f(i)_f\}^x}{\{f(i)_r\}^x} \qquad \ldots(5.3.1)$$

$$\therefore \quad x = \frac{\log (w_f/w_r)}{\log \{f(i)_f / f(i)_r\}} \qquad \ldots(5.3.2)$$

The intensity exponent, x, may therefore be obtained from equation (5.3.2) by measuring the rate of reaction at different intensities of irradiation.

5.4. Results.

5.4.1. Rate - time relationships

For each polymerisation reaction performed in this present work, a graph of meniscus level in the stem against time was drawn. From this, the rate of reaction at any time could be calculated.

FIG. 7

SHAPE OF THE CONTRACTION – TIME CURVES OBTAINED IN THERMAL POLYMERISATIONS.

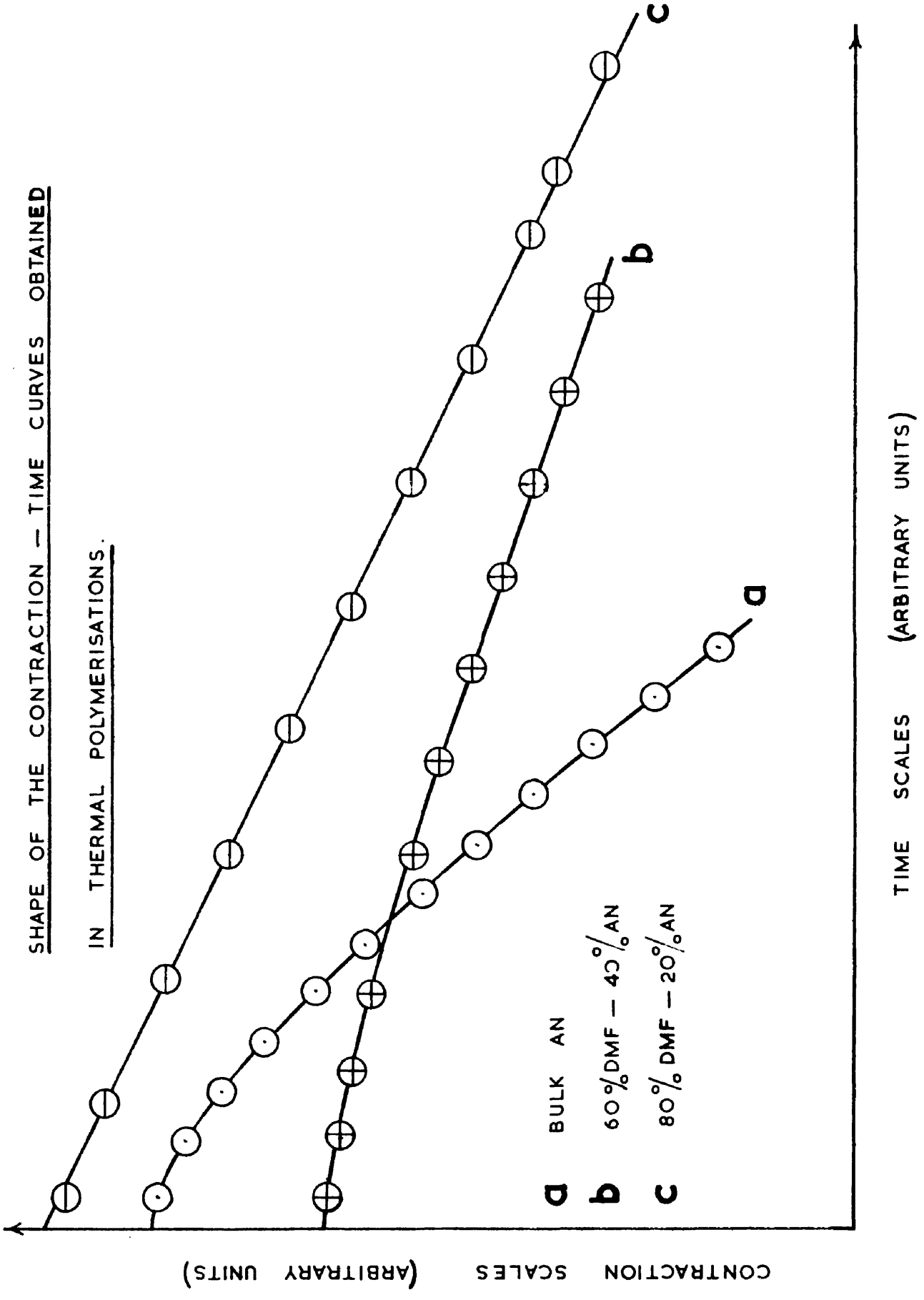
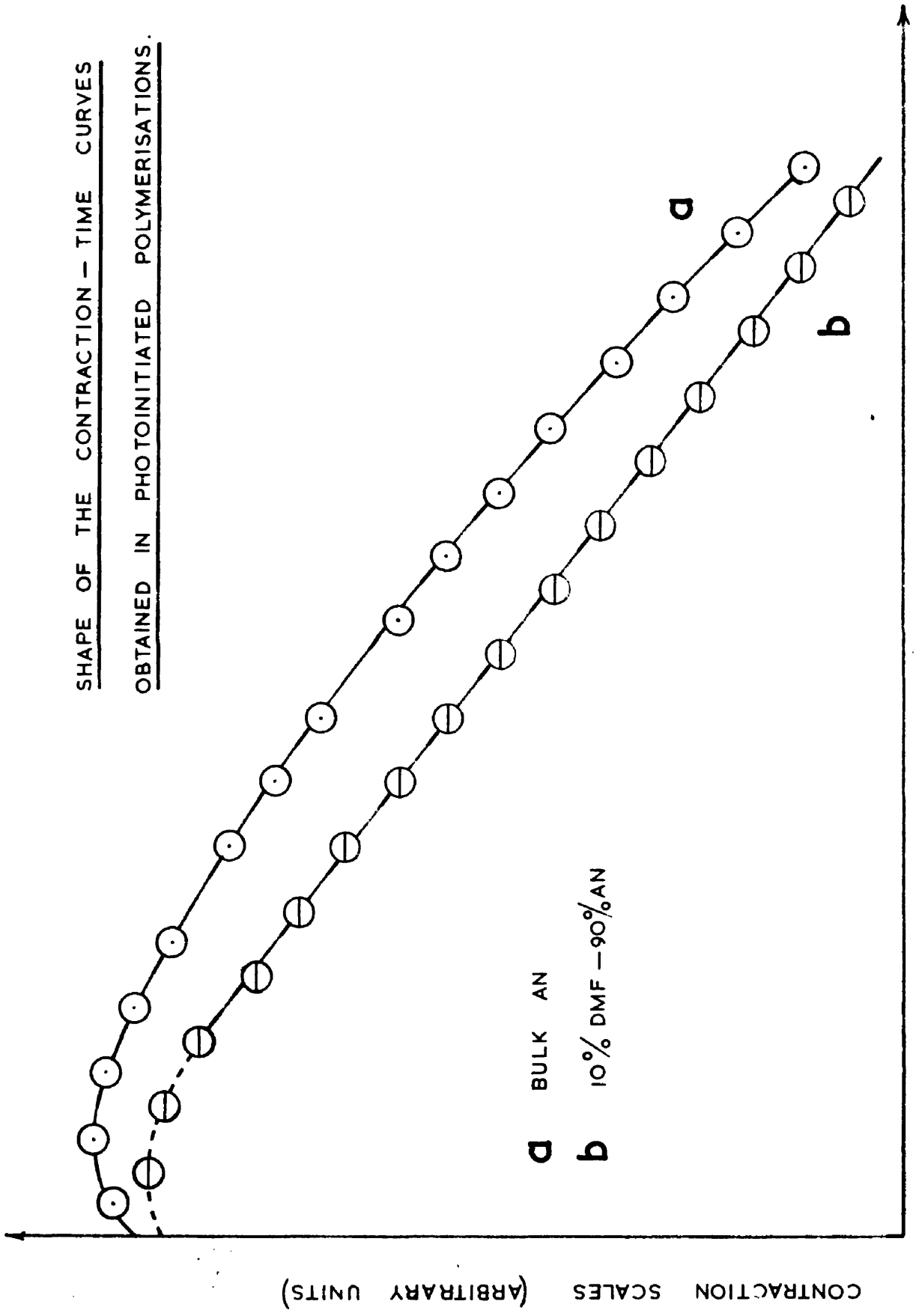


FIG. 8


SHAPE OF THE CONTRACTION – TIME CURVES
OBTAINED IN PHOTOINITIATED POLYMERISATIONS.
a BULK AN
b 10% DMF – 90% AN
a
b
CONTRACTION SCALES (ARBITRARY UNITS)
TIME SCALES (ARBITRARY UNITS)

For the polymerisations of acrylonitrile in DMF - AN mixtures, the following observations were made. With mixtures containing 10% or 20% of acrylonitrile (by volume), polymerisation took place in a homogeneous medium. With a 70% DMF - 30% AN mixture, a faint cloudiness was noted at around 15% conversion. The initial stages of the reaction with a 60% DMF - 40% AN mixture were homogeneous but, after only a low percentage conversion, the reaction mixture became turbid. Heterogeneous polymerisation was observed at all stages of reaction in DMF - AN mixtures containing more than 40% of acrylonitrile.

For the thermal polymerisations, an accelerating rate was found in all reaction mixtures containing more than 40% by volume of acrylonitrile, i.e. in all the heterogeneous polymerisations. A typical curve obtained for the bulk polymerisation is shown in Fig. 7(a). For the 60% DMF - 40% AN mixture, the rate time curve approximated closely to a straight line -Fig.7(b)-whilst, in the homogeneous region, the rate - time relation was linear in the early stages of the reaction and then the rate decreased due to depletion of monomer-Fig.7(c).

In the photochemical polymerisation of acrylonitrile, a less pronounced acceleration in rate was observed as the reaction progressed-Fig.8(a). Addition of even 10% of DMF produced

a linear rate - Fig.8(b) - and the photoinitiated polymerisations of acrylonitrile in reaction mixtures containing more than 10% DMF gave linear relationships between the rate of reaction and the time of irradiation.

It was also found that the addition of bromotrichloromethane to an acrylonitrile polymerisation produced a virtually linear plot of rate of reaction against time if the molar ratio of BTCM:AN was greater than 1. At molar ratios of BTCM:AN of around 1:50, an accelerating rate was obtained.

5.4.2. Rate dependence on monomer concentration.

This was found using DMF - AN reaction mixtures containing from 10% to 90% of acrylonitrile (see section 2.3.6.).

For the initial stages of the reaction, the graph of log. (rate of reaction) against log.(monomer concentration) is shown in Fig.9. The absolute value of the rate of reaction was obtained from initial expansion rate data. This gives a value of 1.2 for the monomer exponent.

The results obtained at later stages of the reaction (around 5% to 10% conversion), are shown in Fig.10. From this, it is seen that the rate of polymerisation is proportional to the first power of the monomer concentration when the reaction

takes place in homogeneous conditions. For monomer concentrations greater than 40% by volume, the monomer exponent rises to a value of approximately 2.5.

5.4.3. Rate dependence on initiator concentration in the bulk polymerisation of acrylonitrile.

This was determined using AIBN as a thermal initiator at 60°C (see section 2.3.5.). Due to the acceleration in rate observed as the reaction progressed, there was no steady rate which could be used for comparisons. The rate dependence on initiator concentration quoted below is therefore based on average values of the rate up to 4% and 12% conversion and on the instantaneous values of the rate at these stages.

The plot of log. (rate of reaction) against log. (initiator concentration) is shown in Fig.11 for data at 4% conversion and in Fig.12 for data at 12% conversion. The values of the initiator exponent thus obtained are given in Table 10, together with the corresponding method of obtaining the values for the rate of reaction.

FIG. 9

RATE DEPENDENCE ON MONOMER CONCENTRATION IN THE VERY EARLY STAGES OF THE POLYMERISATION OF ACRYLONITRILE.

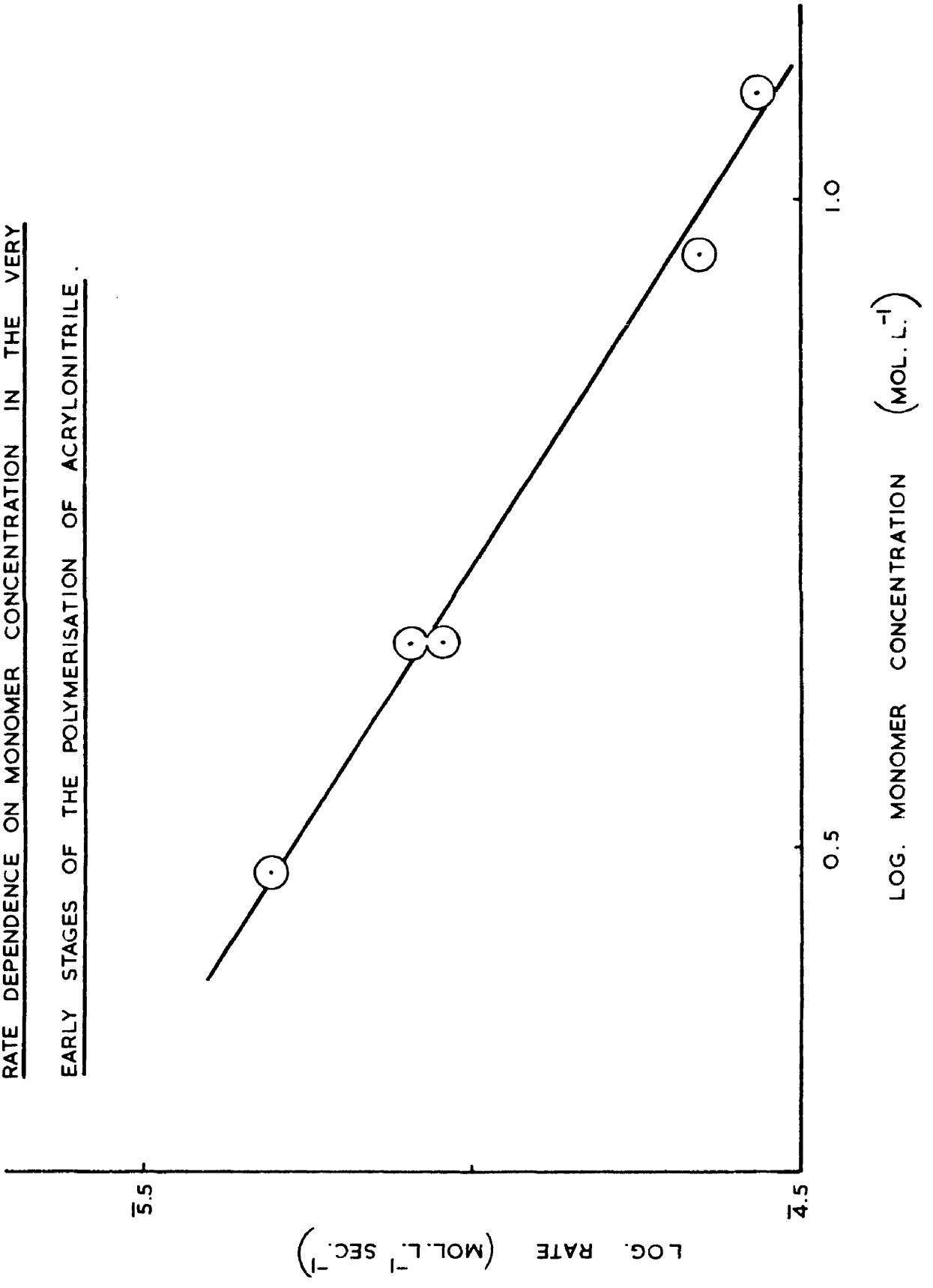


FIG. 10

RATE DEPENDENCE ON MONOMER CONCENTRATION.

AT LATER STAGES OF THE POLYMERISATION.

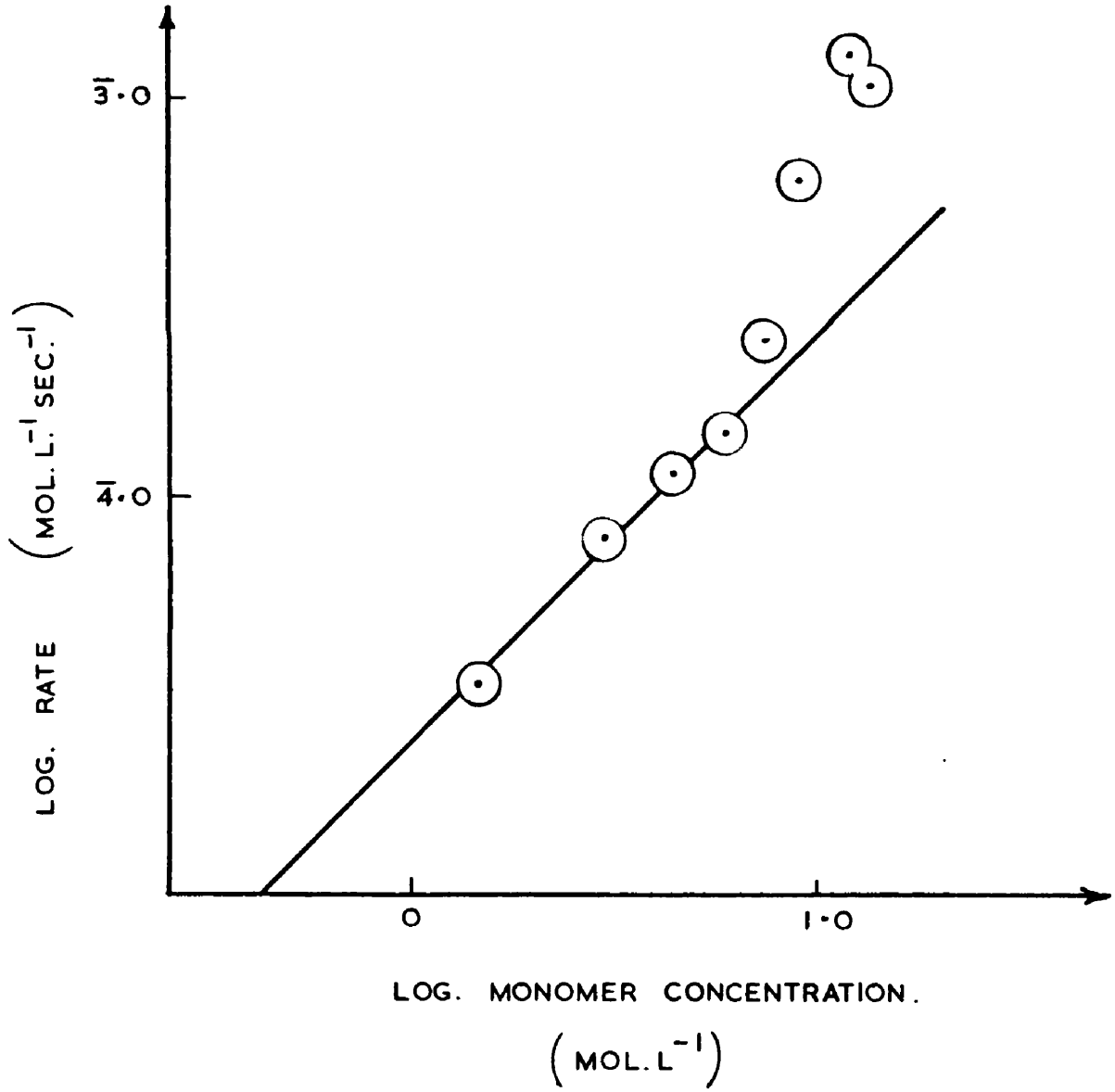


FIG. 11

RATE DEPENDENCE ON AZOBISISOBUTYRONITRILE CONCENTRATION IN THE BULK POLYMERISATION OF ACRYLONITRILE AT 60°C.

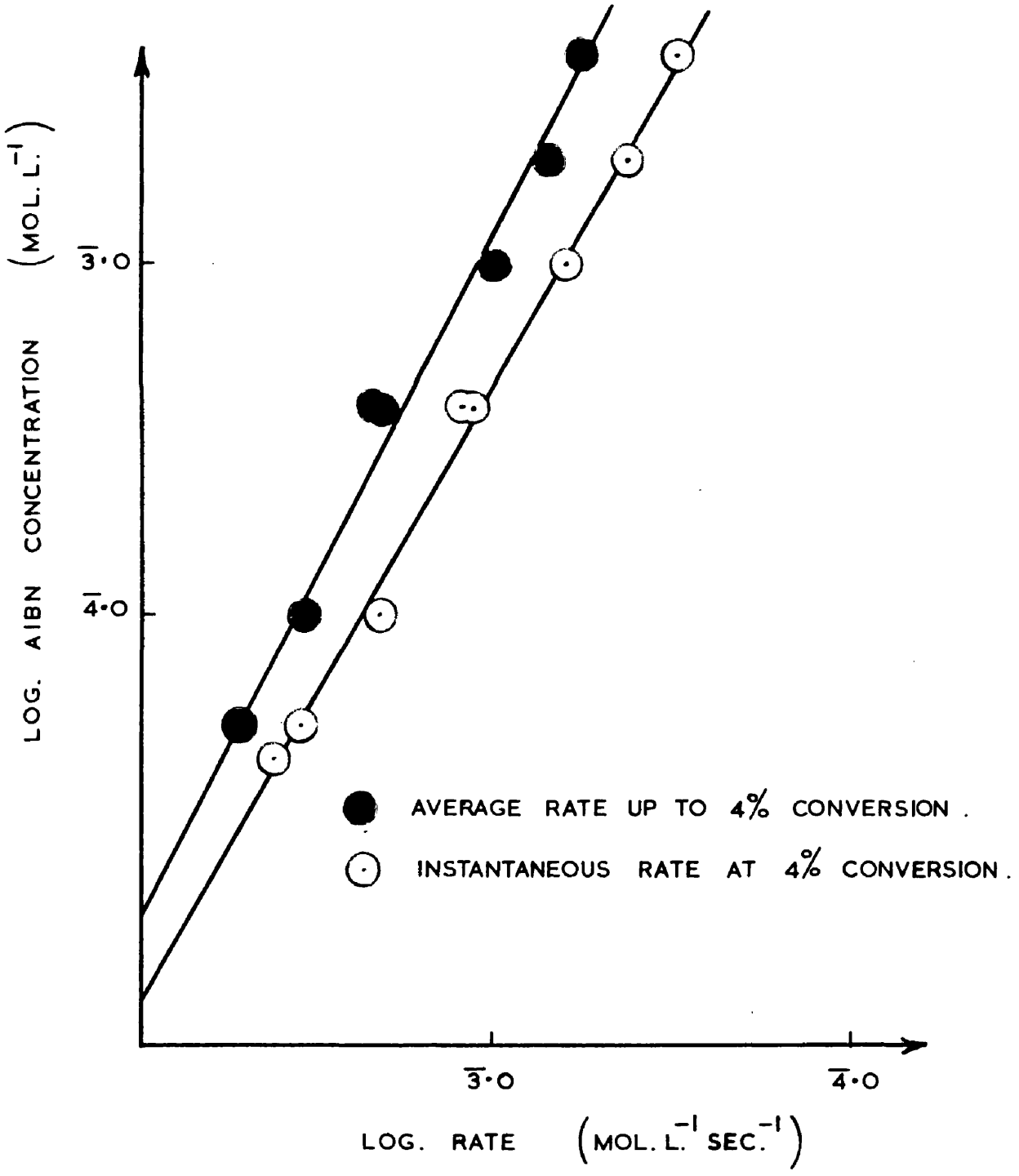


FIG. 12

RATE DEPENDENCE ON AZOBISISOBUTYRONITRILE CONCENTRATION IN THE BULK POLYMERISATION OF ACRYLONITRILE AT 60°C.

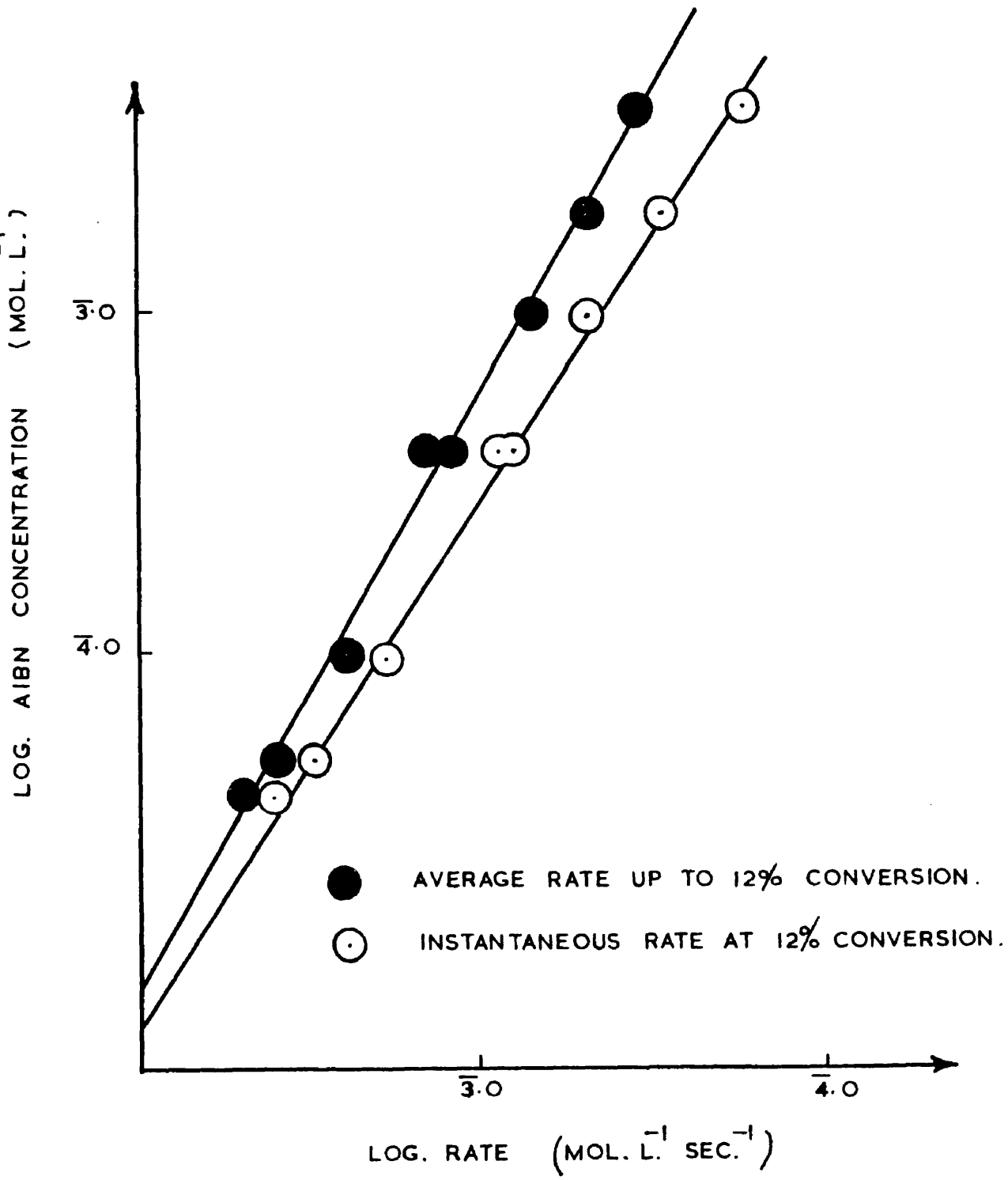


FIG. 13

DEPENDENCE OF RATE OF POLYMERISATION IN DMF SOLUTION ON THE INITIATOR CONCENTRATION .

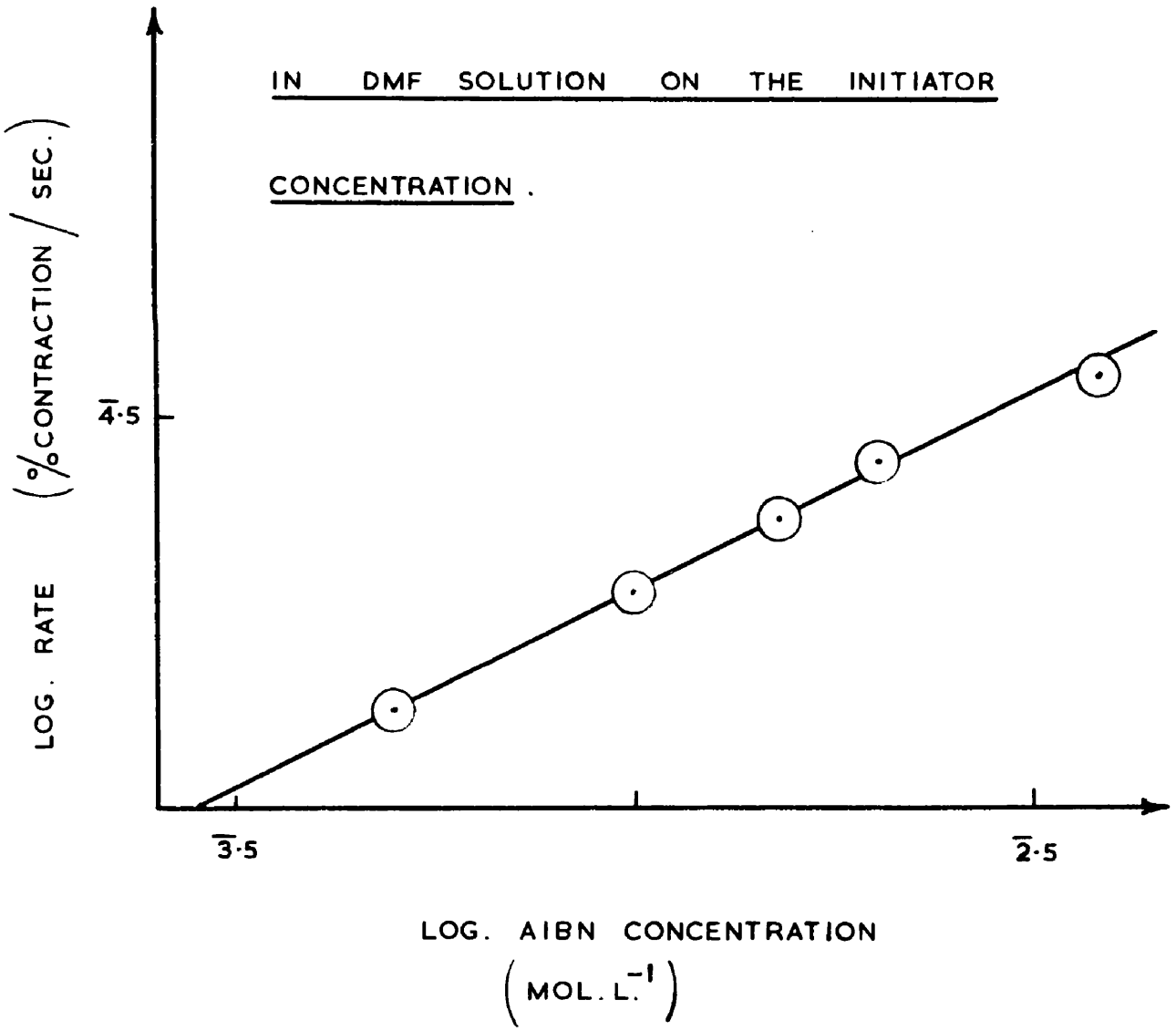


Table 10. Rate dependence on initiator concentration (x_i) in bulk polymerisation of acrylonitrile at 60°C

x_i	Method.
0.51	Av. rate up to 4% conversion.
0.56	Instant. rate at 4% conv.
0.57	Av. rate up to 12% conv.
0.65	Instant. rate at 12% conv.

5.4.4. Rate dependence on initiator concentration in the polymerisation of acrylonitrile in DMF solution.

This series of experiments was carried out at 25°C in an 80% DMF - 20% AN reaction mixture, the polymerisation being photoinitiated (section 2.3.5.).

The graph of log. (rate of reaction) against log. (initiator concentration) is shown in Fig.13. This gives a value of 0.50 for the rate dependence on initiator concentration.

5.4.5. Intensity exponents.

The intensity exponents were calculated using equation (5.3.2.).

Intensity exponents were only determined for three systems and the results are given in Table 11.

Table 11. Average values obtained for the intensity exponents in acrylonitrile polymerisation.

System	Intensity Exponent.
Bulk acrylonitrile	0.70
5% DMF - 95% AN	0.71
80% DMF - 20% AN	0.50

These were all measured using rate data obtained from the non-stationary state measurements when the percentage conversion of monomer into polymer was small.

For later stages of reaction in the photopolymerisation of bulk acrylonitrile (around 10% conversion), intensity exponents as high as 0.91 were obtained.

5.5. Discussion.

5.5.1. Rate - time relationships.

In section 5.4.1. it is stated that the rate of reaction in the bulk polymerisation of acrylonitrile is not constant as

the reaction progresses. This immediately invalidates the traditional kinetic scheme derived by assuming steady state conditions. If, however, the rates are measured instantaneously and not as an average over a given length of time, then equations similar to (5.1.8) and (5.1.11) can be applied to give a close approximation to a true quantitative kinetic analysis. Measurement of the instantaneous rate in the reactions described in this chapter involves drawing a tangent to a curve whose equation is unknown. To try to obtain linear plots from which some rate relationship might have been more easily calculated, the graphs of the log. (contraction) against time and against log. (time) were drawn. The increasing gradient in these curves was equally pronounced.

The rates of reaction have therefore always been measured at a stated percentage conversion and, when comparison between two runs was required, compared to the rate obtained at the same percentage conversion in the other run.

Thus, in the series of reactions to evaluate the rate dependence on initiator concentration - section 5.4.3. - only the results obtained by taking instantaneous rates should be noted. Some work has been published[14,16] in which average rates have been taken and this has led to false values for the initiator

and monomer exponents and for the overall energy of activation.

The acceleration in rate obtained in the heterogeneous polymerisation is now a commonly accepted feature of this reaction. The effect of DMF and BTCM on the shape of the rate - time curve is also in agreement with published data for similar systems. Breitenbach & Schindler[69] have shown that addition of carbon tetrabromide to a vinyl chloride polymerisation produces a linear rate instead of an accelerating one. Bamford & White[70] have studied the effect of amines and n-butyl mercaptan on the polymerisation of acrylonitrile and have shown that these also give linear rate - time relationships. A more striking example is found in the copolymerisation reaction between maleic anhydride and styrene[71]. It has been shown that an acceleration in rate occurred in heterogeneous conditions whilst a linear rate - time relationship was obtained in the homogeneous reaction.

For photochemical work, the rate of reaction has been calculated from the linear portion of the rate - time curve, the stationary state assumption being valid in this case.

5.5.2 Polymerisation of acrylonitrile in DMF solution

The literature values for the rate dependence on initiator and monomer concentrations are varied. Onyon[20] quoted value of

0.59 and 1.34 for the initiator and monomer exponents respectively in a photosensitised reaction at 25°C, compared to the 0.50 and 1.50 given by Scrinivasan & Santappa[33]. Thomas et al[19] found the value of the monomer exponent to vary from 1.0 to 1.7 but claimed an average value of 1.4 . The initiator exponent was found to be 0.5, their work being carried out with thermal initiation at 60°C. More recent papers by Bamford and co-workers have shown the monomer dependence to be 1.0[21] and the initiator dependence to be 0.5[72].

There is no obvious reason for the wide scatter in these reported results. However, the present work confirms the results of Bamford et al and it can be claimed that the polymerisation of acrylonitrile in DMF solution follows the kinetic scheme in section 5.1.1.

5.5.3. Bulk polymerisation of acrylonitrile.

The results which were obtained for this were not as reproducible as those obtained in the homogeneous polymerisations. The value of the intensity exponent found for the photoinitiated reaction seems rather high and this probably due to the precipitating polymer reducing the intensity of the initiating irradiation. The low results obtained for the initiator

exponent at 60°C support this view.

Values reported in the literature for the initiator exponent vary from 0.50 to around 1.0 . Imoto & Takatsugi[16] stated that the value of the initiator exponent lay between 0.6 and 1.0 but they obtained this result by assuming linear rates after the first few percent conversion. The comparison of rates in this case is meaningless. Similar errors are to be found in the results of Bamford & Jenkins[12], instantaneous rates for comparison being taken at the same time interval from the start of the reaction. The value of 0.50 was reported by Bengough[17] using the non-stationary state thermocouple method. He also showed that the value of the intensity exponent rose as the reaction proceeded and this is in agreement with the present work. Similarly high values of the initiator exponent have been quoted for other heterogeneous systems.[71,73]

The values obtained by the author for the monomer exponent also show an increase as the reaction proceeds. From the value of 1.2 obtained for the monomer exponent and of 0.5 obtained for the initiator exponent[17], it may be claimed that the kinetics of the bulk polymerisation of acrylonitrile in the initial stages of the reaction approximate closely to the scheme suggested in section 5.1.1.

At higher percentage conversions, it is apparent that neither of the kinetic schemes suggested in section 5.5. will explain the mechanism of the bulk polymerisation of acrylonitrile.

The significance of the above results will be discussed in detail in chapter 9.

CHAPTER 6.

Determination of the rate of the initiation reaction using αα'-diphenyl-β-picryl hydrazyl.

Various methods have been employed to determine the rate of initiation of a polymerisation reaction. These include:

(a) Evaluation from rate of polymerisation and molecular weight data.

(b) Direct observation of the rate of breakdown of the initiator e.g. by measuring the nitrogen evolved during the breakdown of AIBN.[74,75]

(c) Measurement of the kinetic chain length using radioactive techniques[76,77] or by some other method of end group assay.[78]

(d) Estimation of the number of radicals produced from the initiator using an inhibitor or radical scavenger.

Only the latter method has been used in this thesis and the relevant theory is given below in section 6.1.

6.1. Theory of the determination of the rate of initiation using inhibition and radical scavenging techniques.

The theory for these two methods is virtually identical, the basic difference between the two methods being that a polymerisation reaction follows the complete removal of the inhibitor whereas the radical scavenger is used in a non-polymerisable solvent.

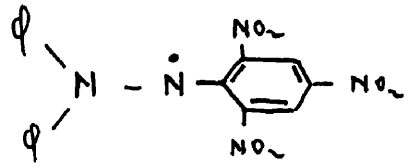
6.1.1. The inhibition method.

In this case, the initiator radicals must react preferentially with the inhibitor so that the polymerisation reaction is completely suppressed. Other conditions which must be observed are that the rate of polymerisation which follows the inhibition period should be the same as the rate of the normal polymerisation in the absence of inhibitor and also, for ideal inhibitor kinetics, the length of the inhibition period must be proportional

to the concentration of inhibitor.

The choice of a suitable substance to inhibit polymerisation is rather limited since many inhibitors are specific in their action e.g. benzoquinone inhibits the polymerisation of vinyl acetate[79] whereas it only retards the polymerisation of methyl methacrylate[80]. This means simply that, in methyl methacrylate polymerisation, the rate of addition of benzoquinone to a growing polymer radical is much less rapid than in the case of vinyl acetate. Thus inhibition and retardation reactions are basically similar, the relative rates of the above two reactions being the main point of difference.

A stable free radical - DPPH - has been used as an inhibitor in this work. This has the structure:



This does not initiate the polymerisation of acrylonitrile.

6.1.2. The radical scavenger method.

The radical scavenger must also react rapidly with the initiator radicals to ensure that recombination does not occur. The rate of removal of the scavenger must be easily followed

and the time taken to remove the radical scavenger must be proportional to its concentration.

DPPH was used as a radical scavenger in the present work and the determination has been performed using solutions of AIBN in benzene and chloroform. DPPH in organic solvents has a distinctive purple colour and the products of its reaction with AIBN have absorbtion spectra which differ widely from that of DPPH. Thus, the rate of removal of DPPH is readily measured spectrophotometrically and this was performed in the above two solvents and also in the monomer.

The interpretation of this rate of removal is not quite so simple. Bawn & Mellish[81] have assumed that each DPPH radical reacted with one initiator radical but other authors[32,82] have questioned the simplicity of this assumption. It is clear that, although the values obtained for the rate of initiation using DPPH as an inhibitor or radical scavenger must be interpreted with caution, the errors involved in this determination are probably no worse than those obtained by the other methods available at present.

In this work, the rate of removal of DPPH has been assumed to equal the rate of production of radicals from the initiator i.e.

an inhibitor and a radical scavenger efficiency of 100% has been assumed. This is probably unjustified but it provides a simple bais for the correction of this experimental data when further information on the reactions of DPPH becomes available.

To calculate the rate of initiation from this data, an initiator efficiency of 75% has been assumed[46]. This may be rather high since Onyon[62] has quoted a value of 55% and a recent paper of Bevington & Eaves[83] has claimed efficiencies of 47% for solution polymerisation and 50% for heterogeneous polymerisation (in benzene). The latter two values, found using a tracer method, are based on the assumption that each polymer molecule contains a fragment of initiator, i.e. does not take account of indirect initiation. This limitation does not apply to the ferric chloride method used to obtain the value of 75% for the initiator efficiency.

It is claimed that ferric chloride acts as an ideal retarder in the thermally initiated polymerisation of acrylonitrile[46]. Attempts were made to apply this method to the photopolymerisation at 25°C and the study of this reaction is discussed in Part II of this thesis.

FIG. 14

TYPICAL DETERMINATION OF THE RATE OF REMOVAL OF DPPH IN BENZENE SOLUTION.

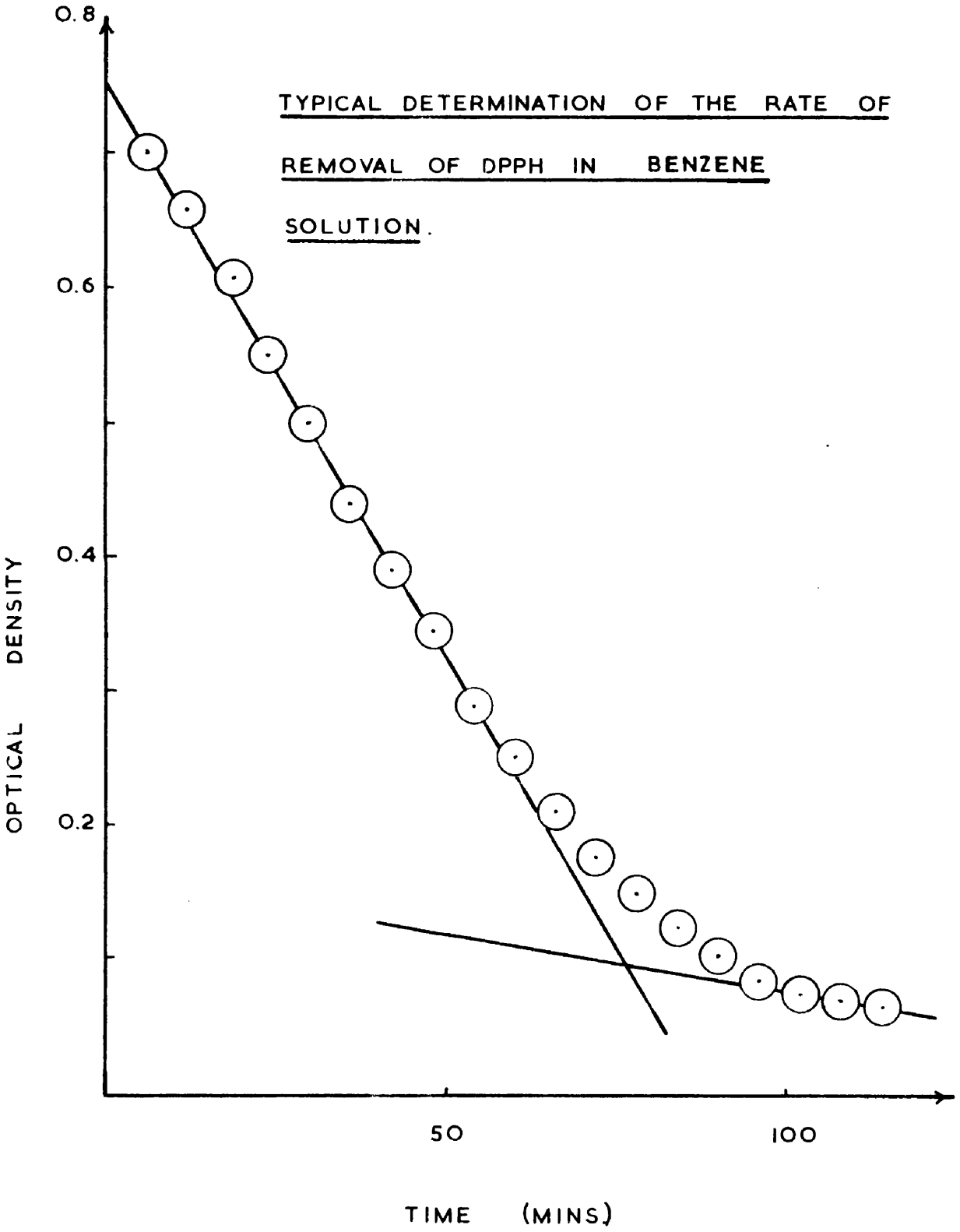


FIG. 15

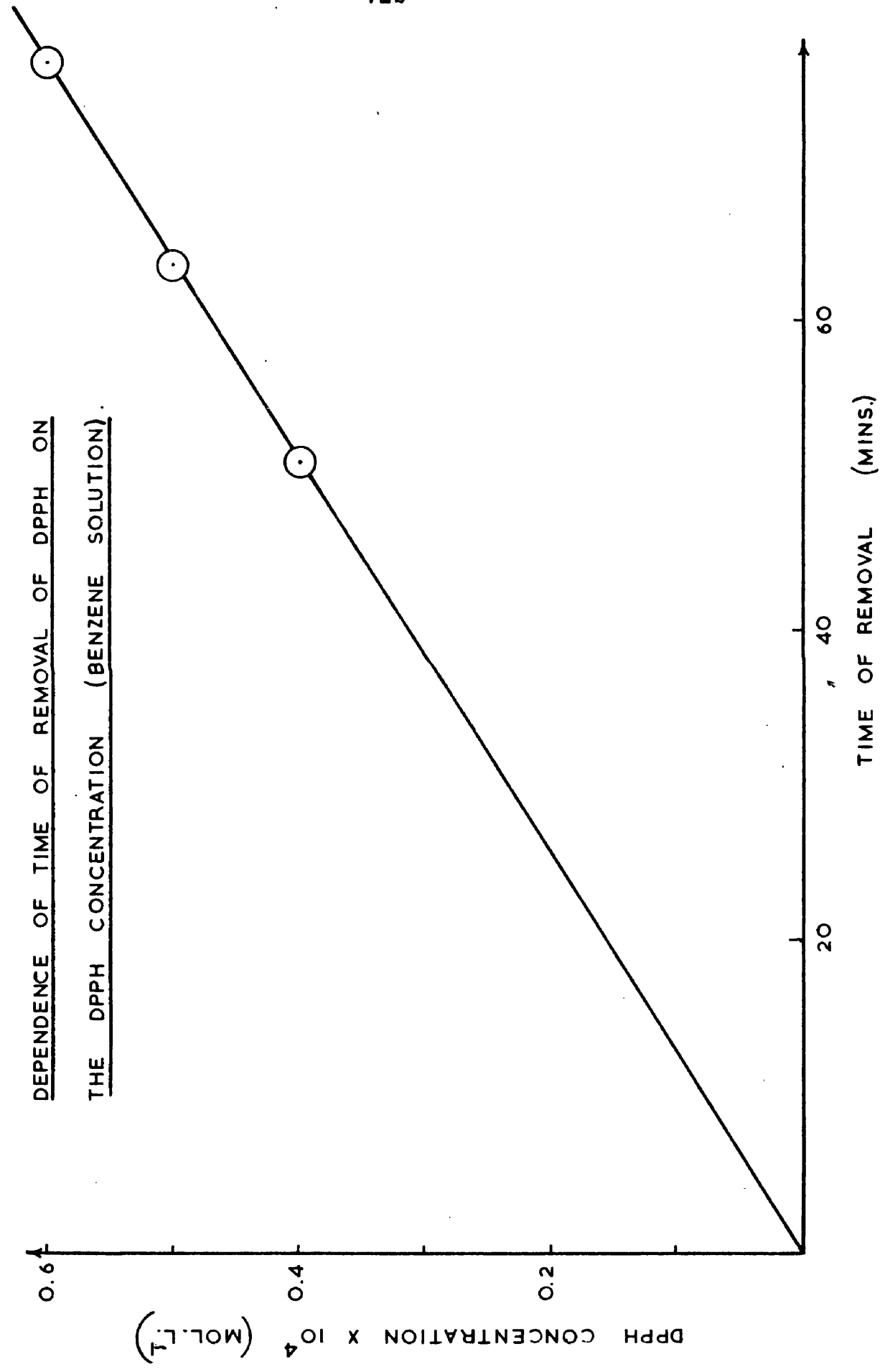

DEPENDENCE OF TIME OF REMOVAL OF DPPH ON
THE DPPH CONCENTRATION (BENZENE SOLUTION).
DPPH CONCENTRATION x 10^4 (MOL.L^{-1})
0.6
0.4
0.2
20
40
60
TIME OF REMOVAL (MINS.)

FIG. 16

DEPENDENCE OF THE RATE OF REMOVAL OF DPPH ON THE AIBN CONCENTRATION (BENZENE SOLUTION).

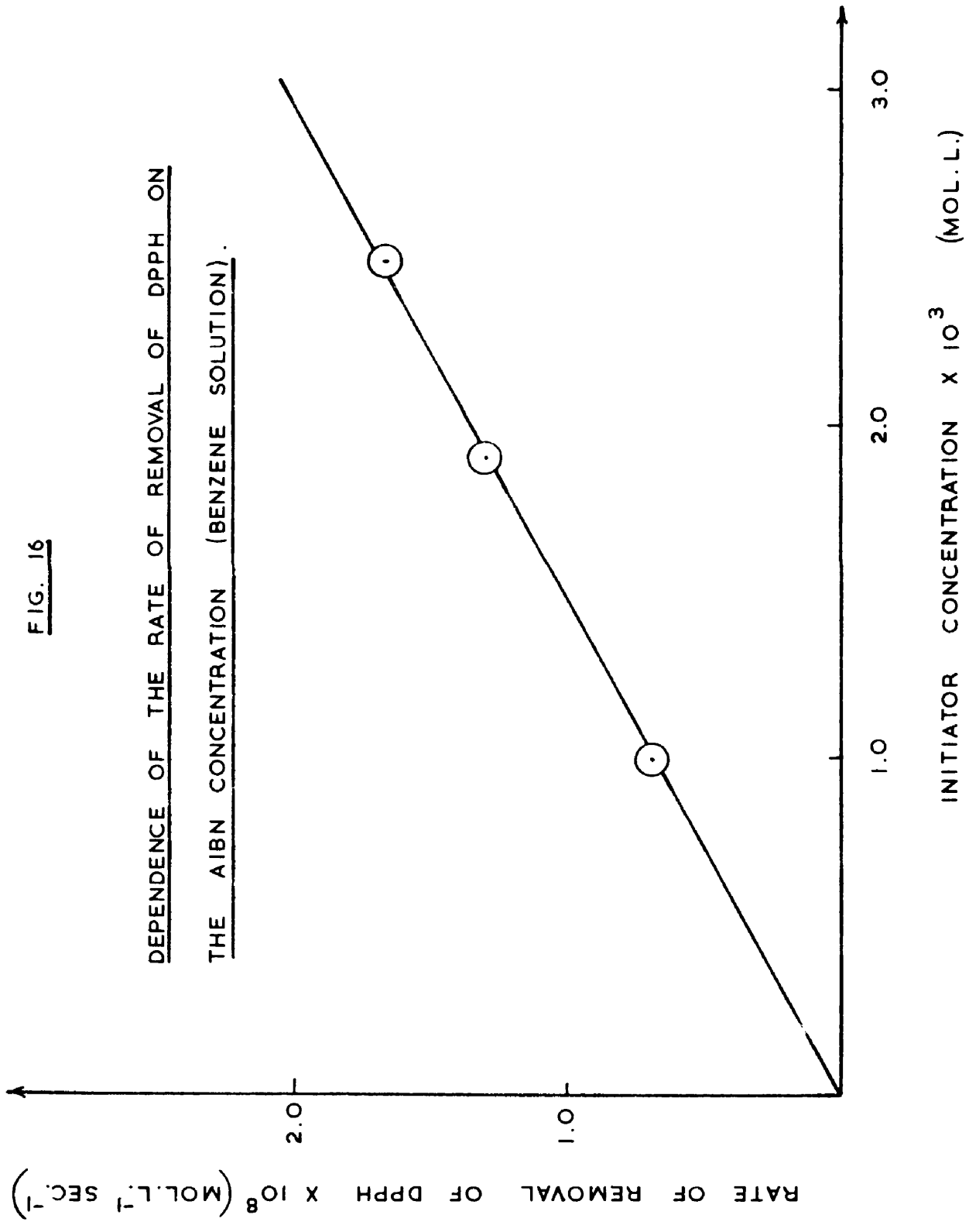


FIG. 17

DIRECT DETERMINATION OF THE INHIBITION PERIOD IN THE BULK POLYMERISATION OF ACRYLONITRILE.

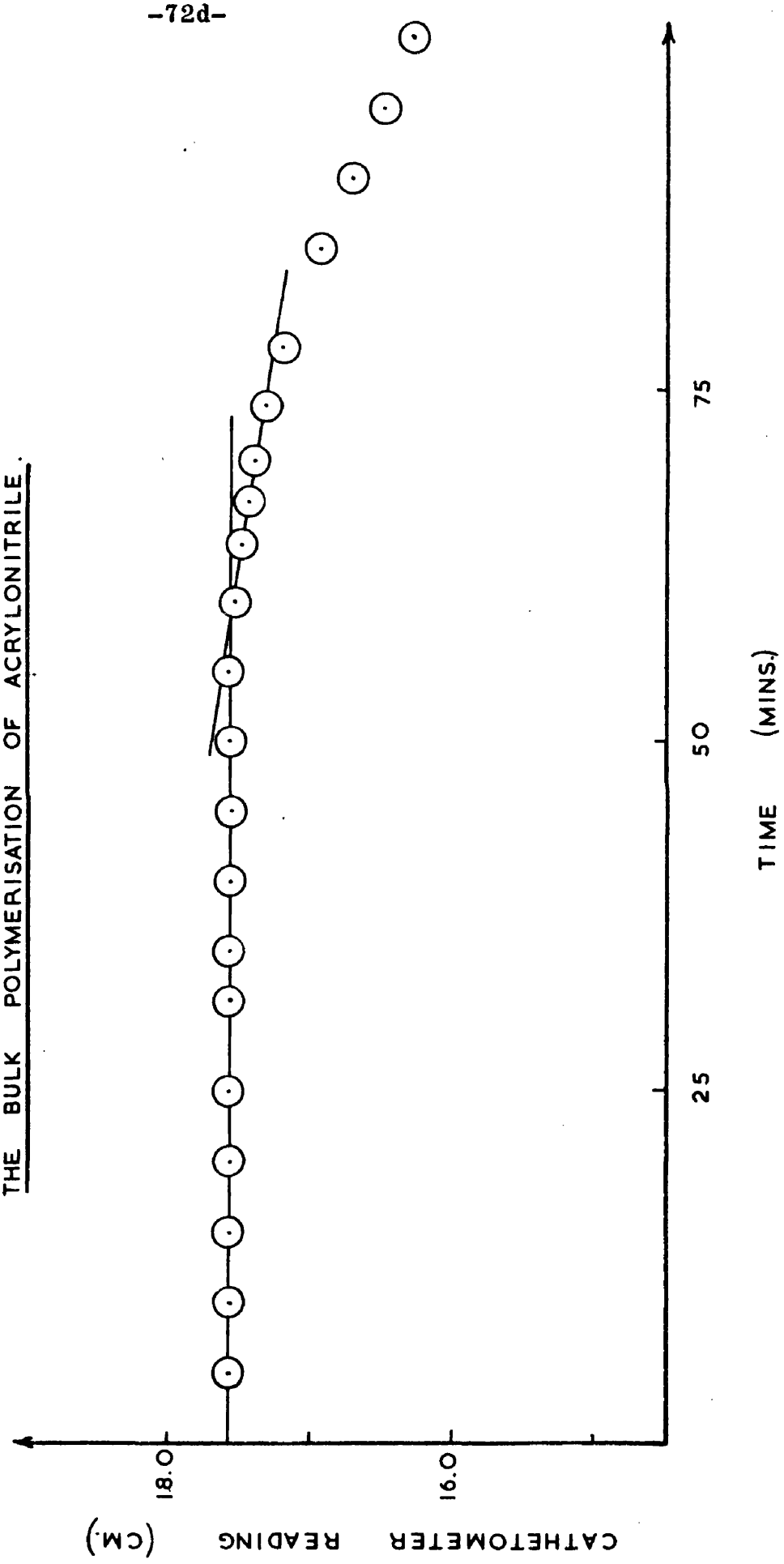
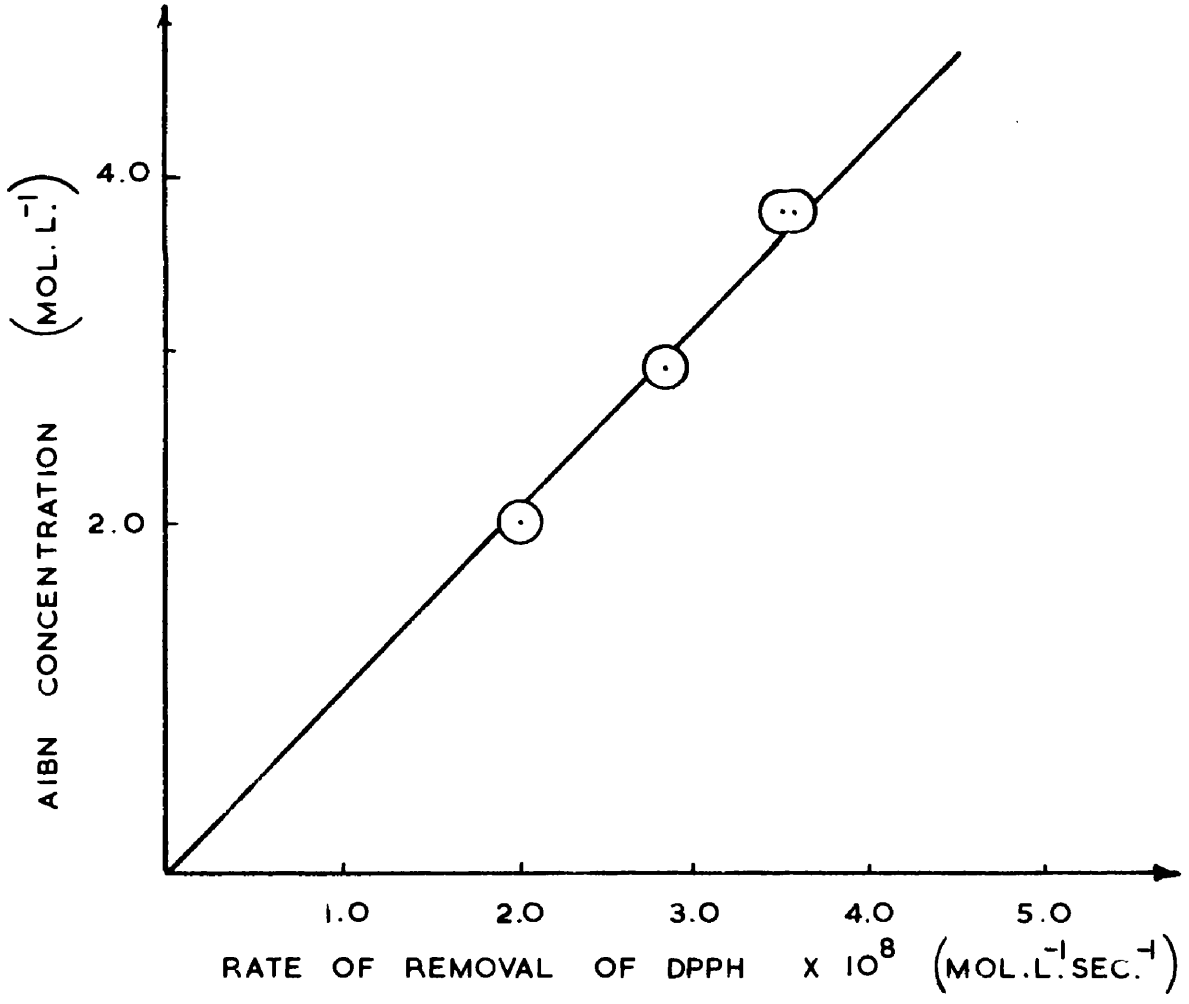


FIG. 18

DEPENDENCE OF THE RATE OF REMOVAL OF DPPH ON THE AIBN CONCENTRATION USING THE DIRECT INHIBITION METHOD.



6.2. Results.

6.2.1. Rate of removal of DPPH in benzene solution using a spectrophotometric method

The rate of removal of DPPH was found from a plot of optical density against time (Fig.14). Fig.15 shows that the rate of removal of DPPH was independent of the concentration of the DPPH. The relation between AIBN concentration and the rate of removal of DPPH was then found (Fig.16).

This gave the rate of removal of DPPH as 1.14×10^{-8} mol.l.$^{-1}$ sec.$^{-1}$ at an initiator concentration of 2.0×10^{-3} mol./l.

6.2.2. Determination of the rate of removal of DPPH in acrylonitrile solution by direct measurement of the inhibition period

In this case, the level of the reactants in the stem of the dilatometer was recorded so that the time - contraction relationship could be accurately found. Since the polymerisation of acrylonitrile exhibits an accelerating rate, it was not possible to adopt the normal method of projection to obtain the inhibition period. This was therefore taken as the time at which a

contraction in volume was first observed. Fig.17 shows a typical experimental curve.

It was found that the duration of the inhibition period depended directly on the DPPH concentration. The relation between AIBN concentration and the rate of removal of DPPH is shown in Fig.18.

The rate of removal of DPPH was found to be 1.63×10^{-8} mol./l.$^{-1}$sec.$^{-1}$ at an initiator concentration of 2.0×10^{-3} mol./l.

6.2.3. Determination of the rate of removal of DPPH in acrylonitrile solution using a spectrophotometric method.

A typical plot of the optical density of the reaction mixture against time is shown in Fig.19. The graph of DPPH concentration against the time taken to remove the DPPH is shown in Fig.20. It is seen that, although the graph is linear, it does not pass through the origin. However, the graph of AIBN concentration against rate of removal of DPPH (Fig.21) was linear and also passed through the origin.

This gave the rate of removal of DPPH as 3.34×10^{-8} mol. l.$^{-1}$sec.$^{-1}$ at an initiator concentration of 2.0×10^{-3} mol./l.

6.2.4. Determination of the rate of removal of DPPH in an 80% DMF - 20% AN solution by direct measurement of the inhibition period.

This series of experiments was not successful. On addition of DMF to DPPH, the purple colour of the DPPH changed immediately to a colour similar to that obtained on complete reaction of DPPH in the above systems. Irradiation for periods of up to 100 minutes produced no polymerisation. When polymerisation eventually did take place, the rate was 1.31×10^{-5} mol.l.$^{-1}$ sec.$^{-1}$ compared to the rate of 4.92×10^{-5} mol.l.$^{-1}$ obtained in the absence of DPPH.

The rate of removal of DPPH was 0.484×10^{-8} mol.l.$^{-1}$sec.$^{-1}$ with an initiator concentration of 2.0×10^{-3} mol./l.

6.2.5. Rate of removal of DPPH in chloroform solution using a spectrophotometric method.

Fig.22 shows the typical shape of curve obtained by plotting the optical density of the solution against the time of irradiation.

Both the graph of the time taken for complete removal of DPPH against DPPH concentration (Fig.23) and the graph of rate of removal of DPPH against AIBN concentration (Fig.24) were

FIG. 19

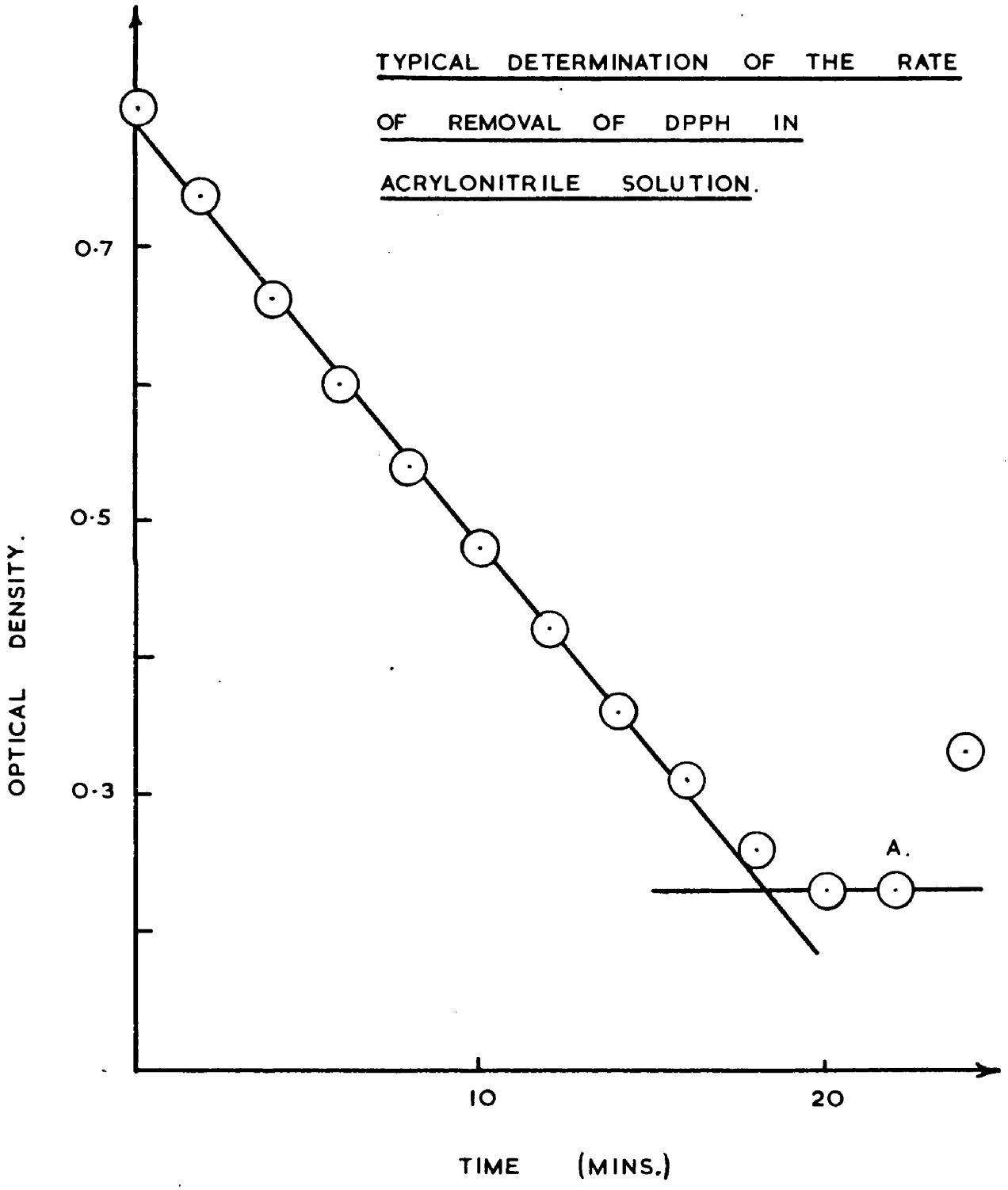

TYPICAL DETERMINATION OF THE RATE OF REMOVAL OF DPPH IN ACRYLONITRILE SOLUTION.
OPTICAL DENSITY.
0·7
0·5
0·3
A.
10
20
TIME (MINS.)

FIG. 20

DEPENDENCE OF TIME OF REMOVAL OF DPPH ON THE DPPH CONCENTRATION (ACRYLONITRILE SOLUTION).

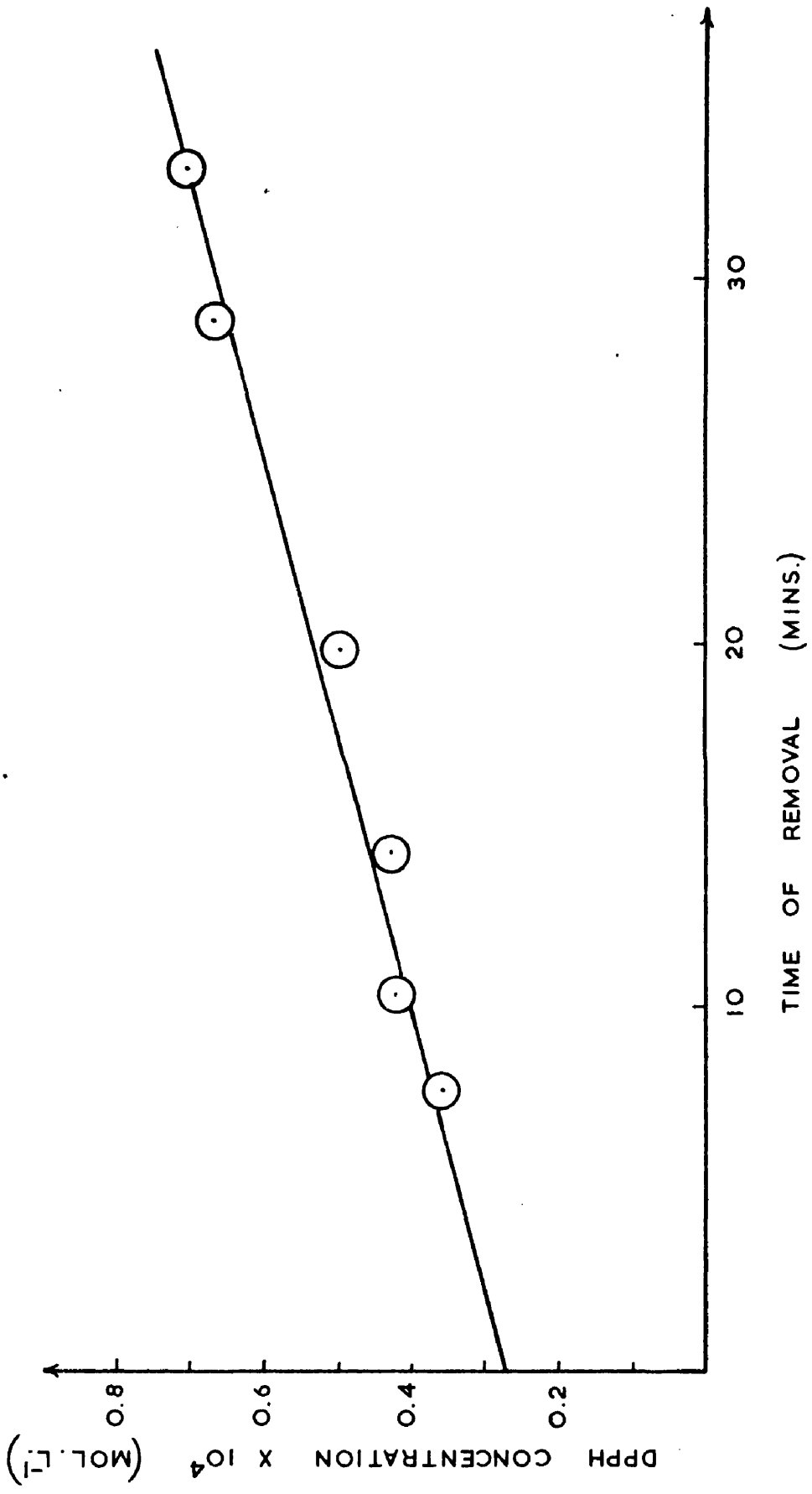


FIG. 21

DEPENDENCE OF THE RATE OF REMOVAL OF DPPH (IN ACRYLONITRILE SOLUTION) ON THE INITIATOR CONCENTRATION.

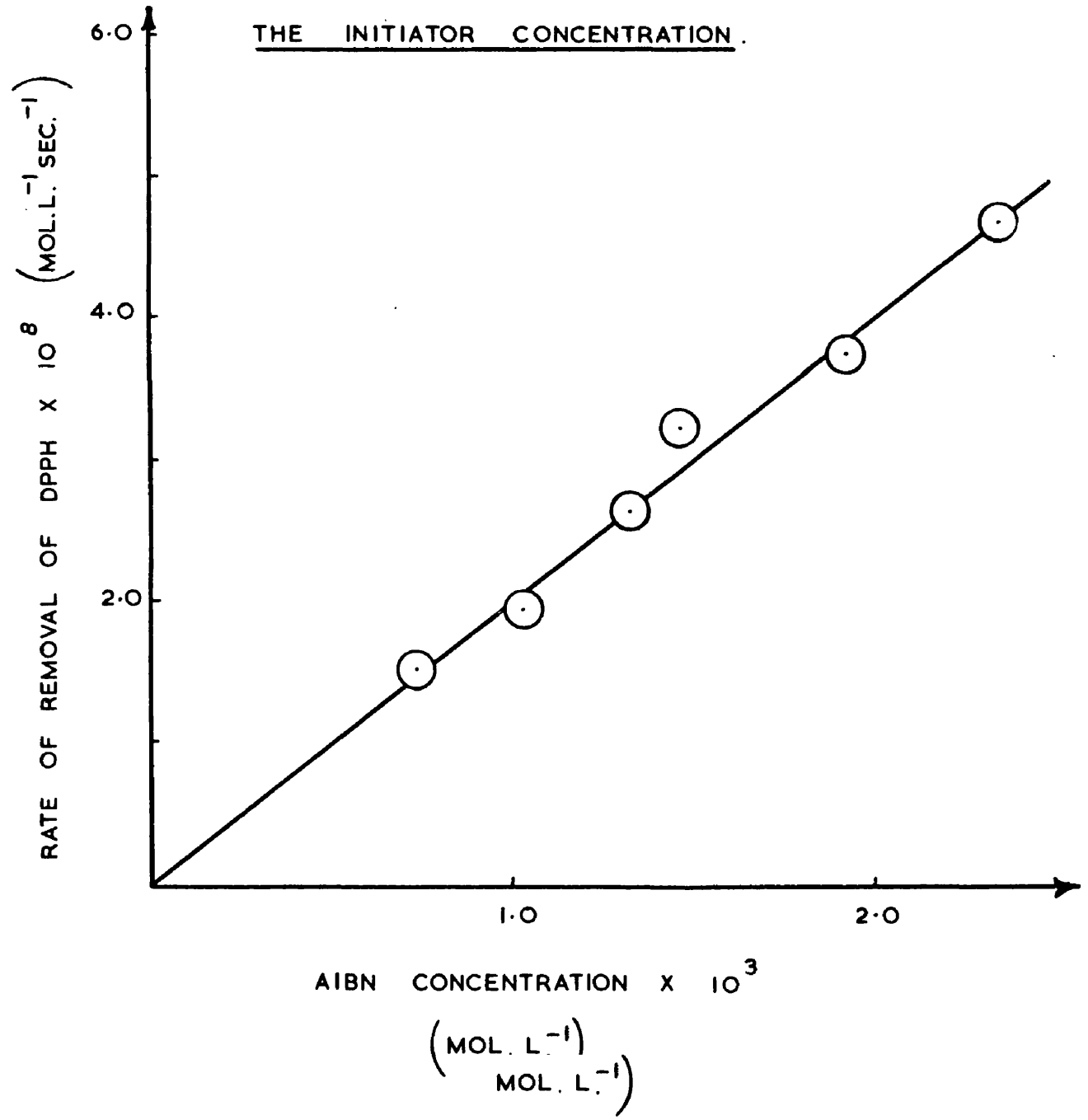


FIG. 22

TYPICAL DETERMINATION OF THE RATE OF REMOVAL OF DPPH IN CHLOROFORM SOLUTION.

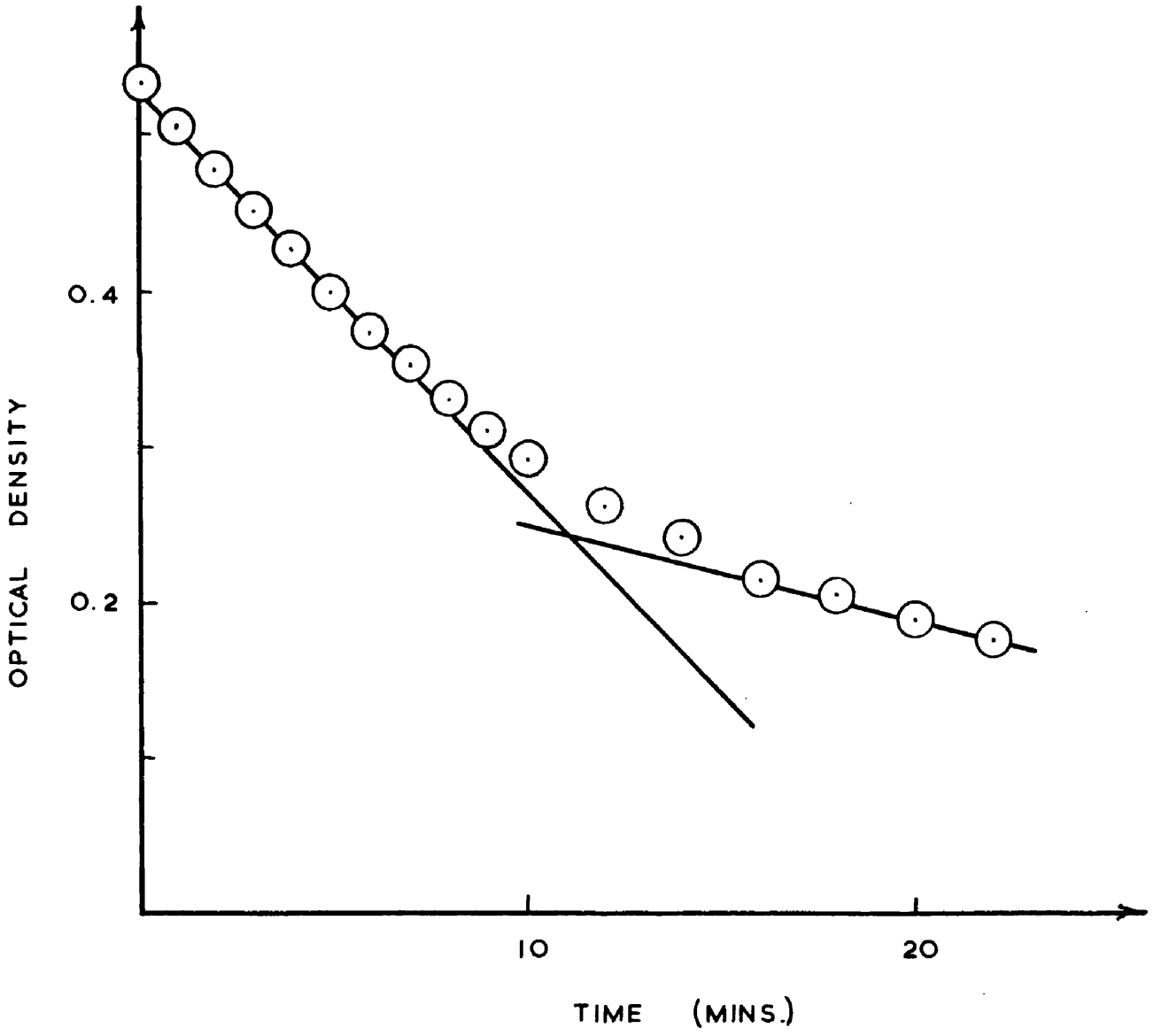


FIG. 23

DEPENDENCE OF THE RATE OF REMOVAL OF DPPH ON THE DPPH CONCENTRATION (CHLOROFORM SOLUTION)

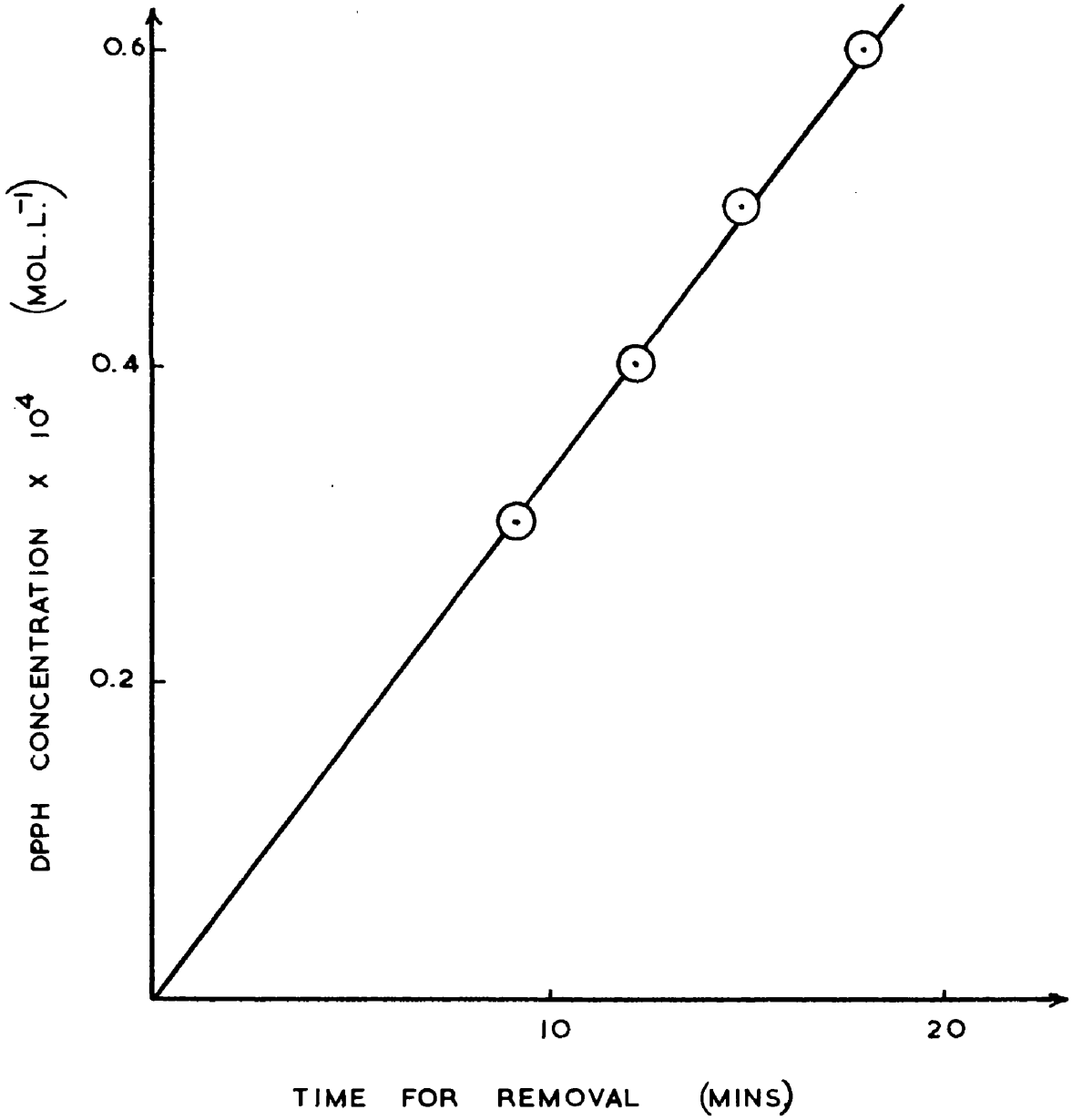
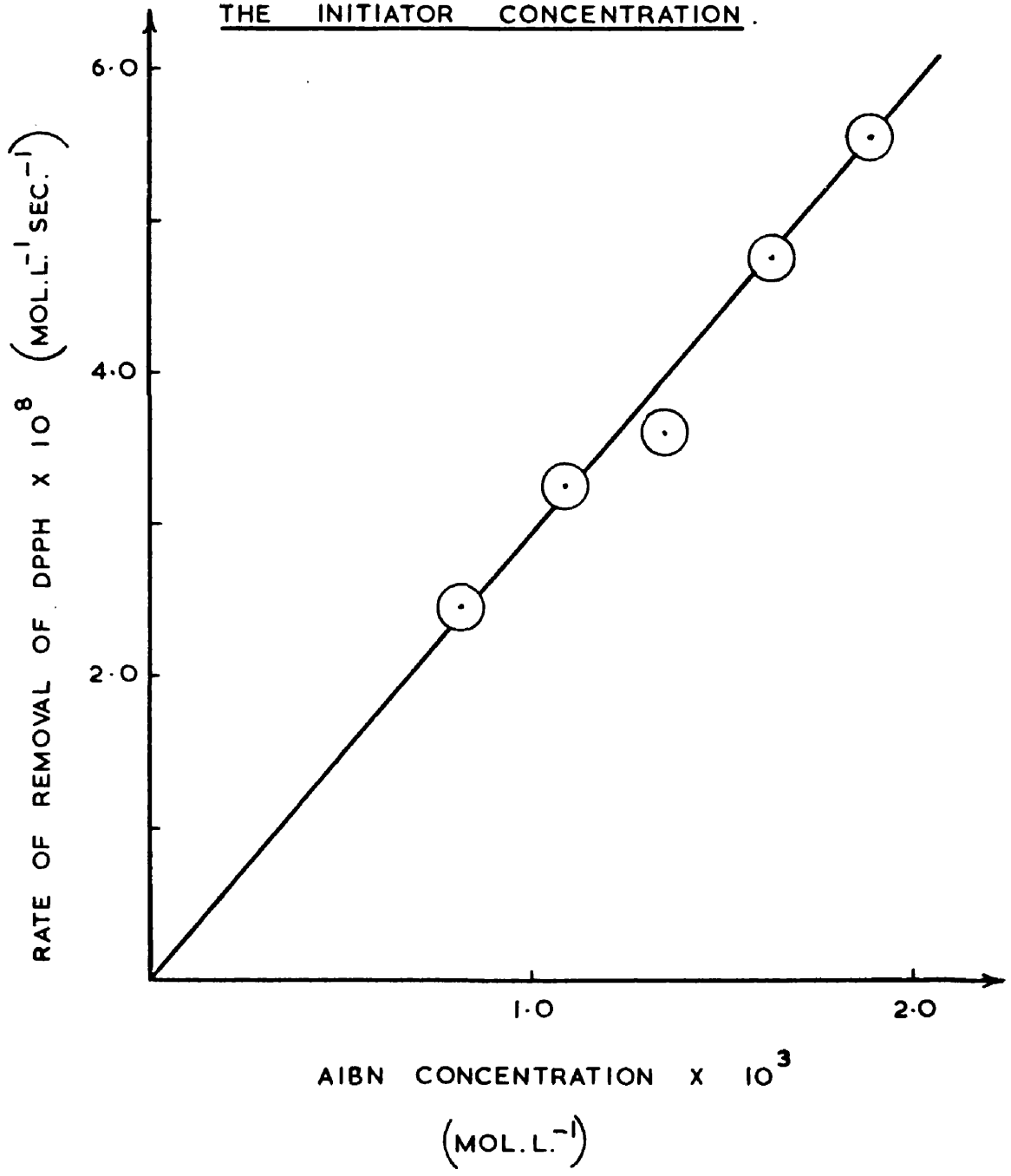


FIG. 24

DEPENDENCE OF THE RATE OF REMOVAL OF DPPH (IN CHLOROFORM SOLUTION) ON THE INITIATOR CONCENTRATION.



linear and passed through the origin.

The rate of removal of DPPH was found to be 4.85×10^{-8} mol. $l.^{-1} sec.^{-1}$ at an initiator concentration of 2.0×10^{-3} mol./l.

6.2.6. Blank Experiments.

Mixtures containing only solvent and DPPH were irradiated and the rate of removal of DPPH was measured spectrophotometrically. In each case, the rate of removal of DPPH was negligible compared to the rate in the presence of AIBN as initiator.

6.2.7. Values for the ratio of the rates of removal of DPPH in the above solvents.

$$\frac{\text{Rate of removal of DPPH in chloroform}}{\text{Rate of removal of DPPH in benzene}} = \frac{4.25}{1} \qquad \ldots(6.2.1)$$

$$\frac{\text{Rate of removal of DPPH in chloroform}}{\text{Rate of rem. of DPPH in acryl.(direct)}} = \frac{2.98}{1} \qquad \ldots(6.2.2)$$

$$\frac{\text{Rate of removal of DPPH in chloroform}}{\text{Rate of rem. of DPPH in AN (spectro.)}} = \frac{1.45}{1} \qquad \ldots(6.2.3)$$

In all the above experiments, the initial concentration of the DPPH was checked from a calibration curve relating

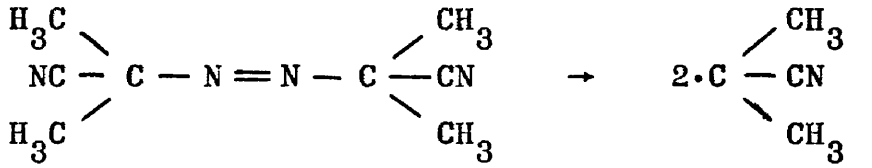
the optical density of the DPPH to its concentration.

6.3. Discussion.

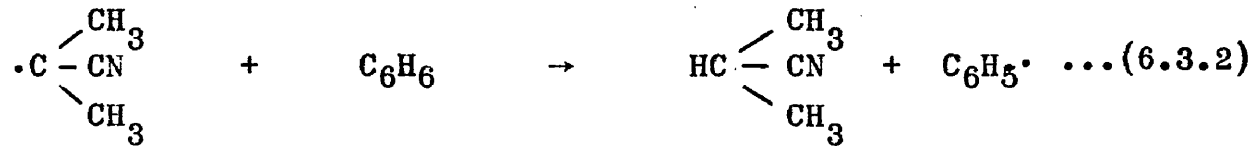
From the above results, it is seen that the experimentally determined value for the rate of removal of DPPH varies with the nature of the solvent. The results will now be discussed in closer detail and possible side reactions suggested. It must be emphasised here that, in such a complex reaction, it is impossible at this stage to give a precise explanation for the wide variation of results and only indirect experimental evidence can be put forward to support the following hypotheses.

6.3.1. Rate of removal of DPPH in benzene solution.

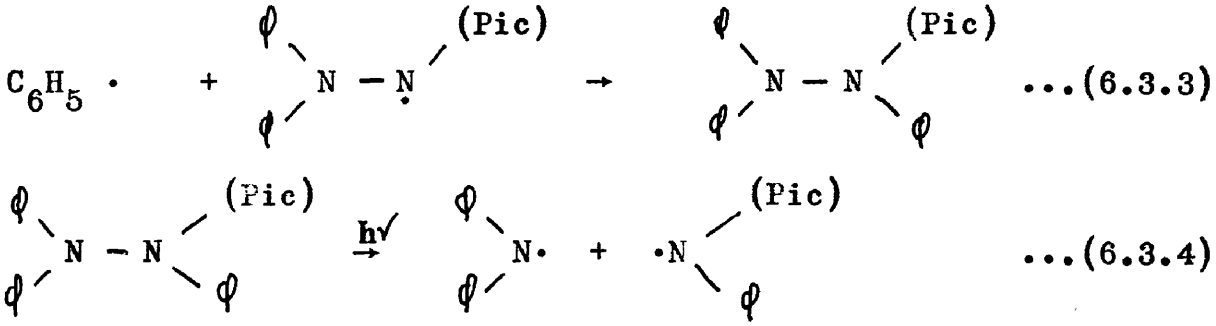
The following mechanism may be operative in this system.



...(6.3.1)



...(6.3.2)



...(6.3.3)

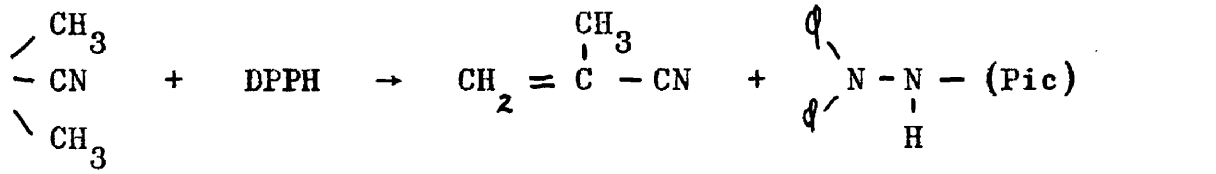
...(6.3.4)

where (Pic) represents the picryl group.

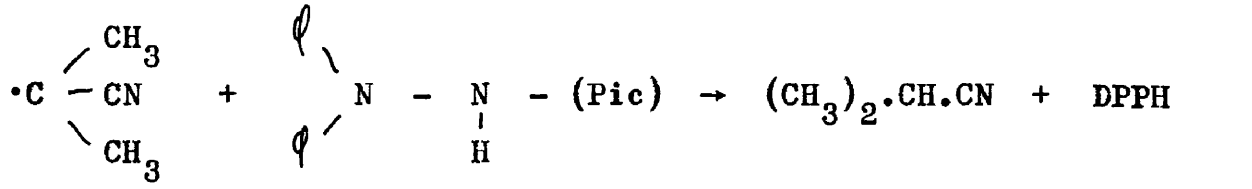
This would make the measured rate of removal of DPPH lower by a factor of three compared to the true rate of production of radicals derived from the AIBN.

Reaction (6.3.1) is well substantiated.[84-89] Since no direct reaction occurred between benzene and DPPH, it is necessary to postulate that hydrogen abstraction occurs by step (6.3.2). A similar type of free radical attack on benzene has been reported by Stockmeyer & Peebles[90] for the polymerisation of vinyl acetate in benzene.

Hammond, Sen, & Boozer[82] have postulated the direct transfer of a hydrogen atom from radicals derived from AIBN to the DPPH:



...(6.3.5)



...(6.3.6)

This would involve the production of appreciable quantities of isobutyronitrile and this was not found in sufficiently large quantities by Bevington[91]. He has also shown[91] that the product of the DPPH - AIBN reaction is not formed by simple combination of the two radical species. Thus it may be that the initiator radical does react with the solvent medium before reacting with the DPPH.

The differing optical densities of the products of the DPPH - AIBN reaction in various solvents also indicates that the initiator is reacting with the solvent. The ratio of the initial optical density to the final optical density is around 2:1 in acrylonitrile and chloroform whilst it has a value of 7:1 in benzene solution. For the rate of removal of DPPH in vinyl acetate and vinyl chloride solutions, values of 3:1 and 6:1 respectively have been obtained[92].

6.3.2. Rate of removal of DPPH in acrylonitrile solution.

In this case, the most obvious side-reaction involves a

hydrogen abstraction reaction. Since no apparent reaction was observed in the blank experiment, direct transfer of a hydrogen atom from the monomeric acrylonitrile can be ignored. The following mechanism can be postulated:

$$\cdot C(CH_3)_2CN + CH_2=CH.CN \rightarrow CN.C.(CH_3)_2.CH_2.\dot{C}H.CN \quad \ldots(6.3.7)$$

This radical may also take part in a modified propagation reaction to give products of the type:

$$CN.C.(CH_3)_2.(CH_2.CH.CN)_n.CH_2.\dot{C}H.CN \quad \ldots(6.3.8)$$

where n is of the order of 1 or 2. A hydrogen abstraction reaction could then occur with the DPPH and a portion of the radicals formed in reactions (6.3.7) and (6.3.8), the remaining radicals combining directly with the DPPH.

$$CN.C.(CH_3)_2.(CH_2.CH.CN)_n.CH_2.CH.CN + DPPH \quad \ldots(6.3.9)$$

$$\downarrow$$

$$CN.C.(CH_3)_2.(CH_2.CH.CN)_nCH = CH.CN + \phi N - \underset{H}{N} - (Pic)$$

i.e. the $\alpha\alpha'$diphenylβpicryl hydrazine is formed. This has been shown to act as an inhibitor by undergoing free radical

oxidation to the DPPH[93]. A similar type of double transfer reaction with polymer radicals has been suggested by Burnett & Cowley[94].

The value for the rate of removal of DPPH as measured by the direct inhibition method was lower than the value obtained by the spectrophotometric method. This was due to the extrapolation used in the latter method to determine the length of the inhibition period. Fig.19 shows the shape of the optical density - time curve and also the extrapolation used to determine the end-point. It was later found that, by centrifuging the reaction mixture at point A, the optical density fell considerably- in the test sample, from 0.45 to 0.22. If the lower value for the optical density had been chosen as the optical density of the product, then the rate of removal of DPPH would have been about 50% lower than the quoted value. This would have given good agreement between the results obtained by the two methods.

Unfortunately, the effect of slight traces of polymer on the optical density was not discovered until this set of experiments had virtually been completed and insufficient data was then available to correct the experimental results.

Thus, the experimental results obtained in acrylonitrile solution using the direct inhibition method were more accurate

than those obtained by the spectrophotometric method. These results, however, may not give a true measure of the rate of production of radicals from the initiator because of the contributions from reactions (6.3.7),(6.3.8), and (6.3.9).

6.3.3. Rate of removal of DPPH in chloroform solution

The rate of removal of DPPH in this solvent was higher than in any of the other solvents. The most obvious reason for this is the direct photolysis of the chloroform to produce radicals which would react with the DPPH. No such reaction was observed (section 6.2.6.) and this agrees with data found by Hill[95]. The reaction of DPPH with AIBN in this solvent appears to be free from complications.

6.3.4. Rate of removal of DPPH in an 80% DMF - 20% AN solution.

This was not studied in detail since the unusual colour obtained on adding DMF to the DPPH indicated that ready reaction was occurring between these two compounds. The product of this reaction is an inhibitor and is presumeably αα'diphenylβpicryl hydrazine.

6.3.5. Rate of initiation.

From the discussion contained in the above sections, it is possible to select the value of the rate of removal of DPPH which corresponds most closely to the actual rate of production of radicals from the AIBN.

For the experiments in benzene, if the postulate in section 6.3.1. is correct, then the rate of production of initiator radicals would be three times the observed rate of removal of DPPH. This would agree with the recent findings of Bawn & Verdin[96] who gave values as low as 0.37 for the efficiency of DPPH in benzene solutions.

However, for the evaluation of the kinetic constants in the following chapter, the rate of production of radicals from AIBN has been taken equal to the rate of removal of DPPH in chloroform solution.

To find the rate of initiation from this data, an initiator efficiency of 75% has been assumed (see section 6.1.). For an initiator concentration of 3.80×10^{-3} mol./l, the value is:

Rate of initiation = 6.91×10^{-8} mol.l.$^{-1}$ sec.$^{-1}$

CHAPTER 7.

The evaluation of the velocity coefficients for propagation and termination in the polymerisation of acrylonitrile using non-stationary state techniques.

In the kinetic analyses quoted in section 5.1., a stationary state was assumed. The methods discussed in this chapter involve the study of the reaction from its initiation up until a steady state is reached.

The practical application of this technique is difficult and it is essential that the following conditions be observed.

(i) The time of the start of the reaction must be

accurately known. This is readily obtained for a photo-initiated reaction.

(ii) An accurate method of measuring the rate of reaction must be available and be of sufficient sensitivity to detect the small variations involved.

(iii) All materials must be rigorously purified so that no initial inhibition periods are obtained.

The second condition is the most difficult to satisfy and methods which have been used include measurement of the rise in temperature in the reaction vessel using a thermocouple[97,98] or a thermistor[99], measurement of the change in the dielectric constant of the reactants[100,101], and interferometry[102].

A dilatometric method of measuring the initial expansion of the reactants[39] was used in the present work and, provided adiabatic conditions are maintained in the reaction vessel, this can be correlated to the absolute rate of reaction (see section 4.4.).

7.1. Theory of the non-stationary state reaction.

Applying the theory due to Burnett[103] to the reaction scheme set out in section 5.1. and assuming the termination

step to be defined by equation (5.1.5),

$$d[R]/dt = I - k_4 [R]^2 \qquad ...(7.1.1)$$

using the same symbols as were defined in section 5.1.

Integration of this gives:

$$\tfrac{1}{2}(k_4 I)^{0.5} \ln \frac{1 + (k_4/I)^{0.5} [R]}{1 - (k_4/I)^{0.5} [R]} = t + c \qquad ..(7.1.2)$$

Substituting the value $[R] = 0$ in equation (7.1.2) gives c, the constant of integration, equal to 0.

$$\text{i.e.} \quad (I/k_4)^{0.5} . \tanh^{-1} (k_4/I)^{0.5} [R] = It \qquad ...(7.1.3)$$

$$\text{or} \quad \tanh^{-1} [R]/[R_s] = (k_4 I)^{0.5} t \qquad ...(7.1.4)$$

Now, let τ be the lifetime of the growing chain:

$$\tau = [R_s]/ k_4 [R_s]^2 \qquad ...(7.1.5)$$

$$\text{or} \quad \tau = 1/(k_4 I)^{0.5} \qquad ...(7.1.6)$$

Substituting this in equation (7.1.4) gives:

$$\tanh^{-1} [R]/[R_s] = t/\tau \qquad ...(7.1.7)$$

$$\text{or} \qquad [R] = [R_s] \tanh t/\tau \qquad \ldots(7.1.8)$$

The rate of removal of monomer at any instant is given by:

$$-d[M]/dt = k_2 [R][M] \qquad \ldots(7.1.9)$$

$$= k_2 [R_s][M] \tanh t/\tau \qquad \ldots(7.1.10)$$

Integration of equation (7.1.10) gives:

$$-\ln ([M]/[M_o]) = (k_2/k_4) \ln \cosh (t/\tau) \qquad \ldots(7.1.11)$$

where $[M]$ is the monomer concentration at any instant, and $[M_o]$ is the initial monomer concentration.

If F is the fraction of monomer which has been converted to polymer, then

$$[M] / [M_o] = 1 - F \qquad \ldots(7.1.12)$$

$$\text{i.e.} \quad -\ln (1 - F) = (k_2/k_4) \ln \cosh (t/\tau) \qquad \ldots(7.1.13)$$

and for $F \ll 1$, as is the case in non-stationary state determinations,

$$-\ln (1 - F) = F \qquad \ldots(7.1.14)$$

$$\therefore \qquad F = (k_2/k_4) \ln \cosh (t/\tau) \qquad \ldots(7.1.15)$$

Thus, when $t \ggg \tau$,

$$F = (k_2/k_4)\left\{\frac{t}{\tau} - \ln 2\right\} \qquad \ldots(7.1.16)$$

Thus, by plotting the fraction of monomer converted to polymer as a function of time, the resultant straight line will intersect the time axis at $\underline{t}$ where $t = \tau \ln 2$. The slope of the line will be $k_2/k_4\tau$ i.e.

$$F/t = k_2/k_4\tau$$

$$\text{or} \quad k_2/k_4 = F\tau/t \qquad \ldots(7.1.17)$$

$$= F\,[M]\,\tau/[M]t$$

$$\text{i.e.} \quad k_2/k_4 = \frac{-d[M]/dt \,.\, \tau}{[M]} \qquad \ldots(7.1.18)$$

This equation may also be derived from normal stationary state kinetics by substituting $1/\tau k_4^{0.5}$ for $I^{0.5}$ in equation (5.1.8).

By using equations (7.1.18) and (5.1.8), values of k_2/k_4 and $k_2/k_4^{0.5}$ are obtained and the individual velocity coefficients can then be calculated.

The above equations only apply to a kinetic scheme such as that described in section 5.1. and where the termination occurs by means of the reaction between two radicals, i.e. where the

initiator and intensity exponents are both 0.50 .

In the dilatometric method[39], the fraction of monomer converted to polymer is estimated by measuring the expansion of the reactants brought about by the release of the heat of polymerisation. When this initial expansion is plotted against time, then the intercept on the time axis is equal to $\tau \ln 2$, the reaction system being treated as an adiabatic one over the initial stages of the reaction.

A similar dilatometric method has been used by Benson & North[104] to determine the rate constants of a chain reaction. The method of calculation in this case is based on the solution of differential equations governing heat flow and the reaction occurring in the system.

7.2. The theory of the modified rotating sector method[45].

In this method, a pseudo-stationary state is attained i.e. a stationary state which is governed by physical processes as well as by chemical reaction rates. The theory of the rotating sector method is derived along similar lines to the non-stationary state theory.

The use of intermittent light to determine velocity

coefficients was first suggested by Briers et al[40] in 1926 but the first significant development to the field of liquid phase polymerisations was in 1945 when several workers[41-44] applied it to the determination of the velocity coefficients in vinyl acetate polymerisation.

Consider a system exposed to intermittent light. For the light period, assuming second order termination (section 5.1.):

$$d[R]/dt = I - k_4 [R]^2 \qquad ...(7.2.1)$$

and, for the dark period:

$$d[R]/dt = - k_4 [R]^2 \qquad ...(7.2.2)$$

Integration of equation (7.2.1) gives the instantaneous value of the concentration of radicals during the light period, i.e.

$$(I/k_4)^{0.5} \tanh^{-1} (k_4/I)^{0.5} [R] = It + c \qquad ..(7.2.3)$$

or $$[R] / [R_s] = \tanh (t/\tau) \qquad ...(7.2.4)$$

This is the equation for the build up of the radical concentration during the light period.

Integration of equation (7.2.2) gives the instantaneous value of the radical concentration during the dark period:

$$1 / [R] = k_4 t + c \qquad ...(7.2.5)$$

The constant of integration will normally be close to zero and may therefore be neglected. The decay equation then becomes:

$$\frac{1}{[R] / [R_s]} = t / \tau \qquad ...(7.2.6)$$

The average concentration of radicals during the light period ($[R_L]$) is found by integrating the radical concentration over the light period:

$$[R_L] = (1/t) \int_{T_2}^{T_1} [R] \, .dt$$

$$= ([R_s]/t) \int_{T_2}^{T_1} \tanh [R_s](k_4 t + c).dt$$

$$= \frac{1}{k_4 t} \ln \left\{ \frac{1 - \tanh^2 [R_s] (k_4 T_2 + c)}{1 - \tanh^2 [R_s] (k_4 T_1 + c)} \right\}^{0.5}$$

$$\text{i.e.} [R_L] = \frac{1}{k_4 t} \ln \left\{ \frac{1 - ([R_2]/[R_s])^2}{1 - ([R_1]/[R_s])^2} \right\}^{0.5} \qquad ..(7.2.7)$$

where $[R_1]$ and $[R_2]$ are the radical concentrations at the beginning and end of the dark period and t is the duration of

the light period.

Similarly, the average value of the radical concentration in the dark period is:

$$[R_D] = \frac{1}{2rk_4t} \ln \frac{[R_1]^2}{[R_2]^2} \qquad \ldots(7.2.8)$$

where r is the ratio of the dark period to the light period and t is again the length of the light period.

The overall average radical concentration, $[R_o]$, for one complete cycle of light period and dark period will therefore be:

$$(r + 1)[R_o] = [R_L] + [R_D]\, r \qquad \ldots(7.2.9)$$

Substituting for $[R_L]$ and $[R_D]$ from equations (7.2.7) and (7.2.8) in equation (7.2.9) gives:

$$(r + 1)[R_o] = \frac{1}{2k_4t}\left\{\ln \frac{1 - ([R_2]/[R_s])^2}{1 - ([R_1]/[R_s])^2} + \ln\left(\frac{[R_1]}{[R_2]}\right)^2\right\} \qquad \ldots(7.2.10)$$

Now, equation (7.2.3) may be rewritten:

$$(1/[R_s])\ \tanh^{-1}[R]/[R_s] = k_4t + c \qquad \ldots(7.2.11)$$

$$\therefore \tanh^{-1}([R_1]/[R_s]) - \tanh^{-1}([R_2]/[R_s]) = k_4 t [R_s] \quad \ldots(7.2.12)$$

Let $$t/\tau = m \quad \ldots(7.2.13)$$

$$\therefore \tanh^{-1}([R_1]/[R_s]) - \tanh^{-1}([R_2]/[R_s]) = m \quad \ldots(7.2.14)$$

From the decay equation (7.2.5),

$$(1/[R_2]) - (1/[R_1]) = k_4 r t \quad \ldots(7.2.15)$$

Also, writing equation (7.2.14) in logarithmic form gives:

$$2\left\{m + \ln \frac{1 + [R_2]/[R_s]}{1 + [R_1]/[R_s]}\right\} = \ln \frac{1 - ([R_2]/[R_s])^2}{1 - ([R_1]/[R_s])^2} \quad \ldots(7.2.16)$$

Substituting in equation (7.2.10) gives:

$$(r + 1)[R_o] = \frac{1}{k_4 t}\left\{m + \ln \frac{1 + [R_2]/[R_s]}{1 + [R_1]/[R_s]} + \ln \frac{[R_1]}{[R_2]}\right\} \quad \ldots(7.2.17)$$

Substituting further the value of $[R_2]$ obtained in equation (7.2.15):

$$(r + 1)[R_o] = \frac{m}{k_4 t}\left\{1 + \frac{1}{m} \ln\left(1 + \frac{rm}{1 + [R_s]/[R_1]}\right)\right\} \quad .(7.2.18)$$

Also, from equations (7.2.12) and (7.2.13),

$$m = k_4 t [R_s] \qquad \ldots(7.2.19)$$

$$\therefore \quad (r+1)\frac{[R_o]}{[R_s]} = 1 + \frac{1}{m} \ln \left\{ 1 + \frac{rm}{1 + [R_s]/[R_1]} \right\} \qquad (7.2.20)$$

For the present work, where the sector used produced equal dark and light periods, equation (7.2.20) becomes:

$$\frac{[R_o]}{[R_s]} = \frac{1}{2} \left\{ 1 + \frac{1}{m} \ln \left\{ 1 + \frac{m}{1 + [R_s]/[R_1]} \right\} \right\} \qquad \ldots(7.2.21)$$

By using equations (7.2.4) and (7.2.5), curves showing the rate of build up and the rate of decay of the radical concentration were constructed. These are shown in Figs. 25 and 26 respectively.

When the duration of the light and dark periods is large compared to the radical lifetime, τ, then the radical concentration will decrease considerably during the dark period. Thus, with long flash times and using a sector giving equal light and dark periods, the total irradiation incident on the system will be 50% of that under steady

FIG. 25

BUILD UP OF RADICAL CONCENTRATION.

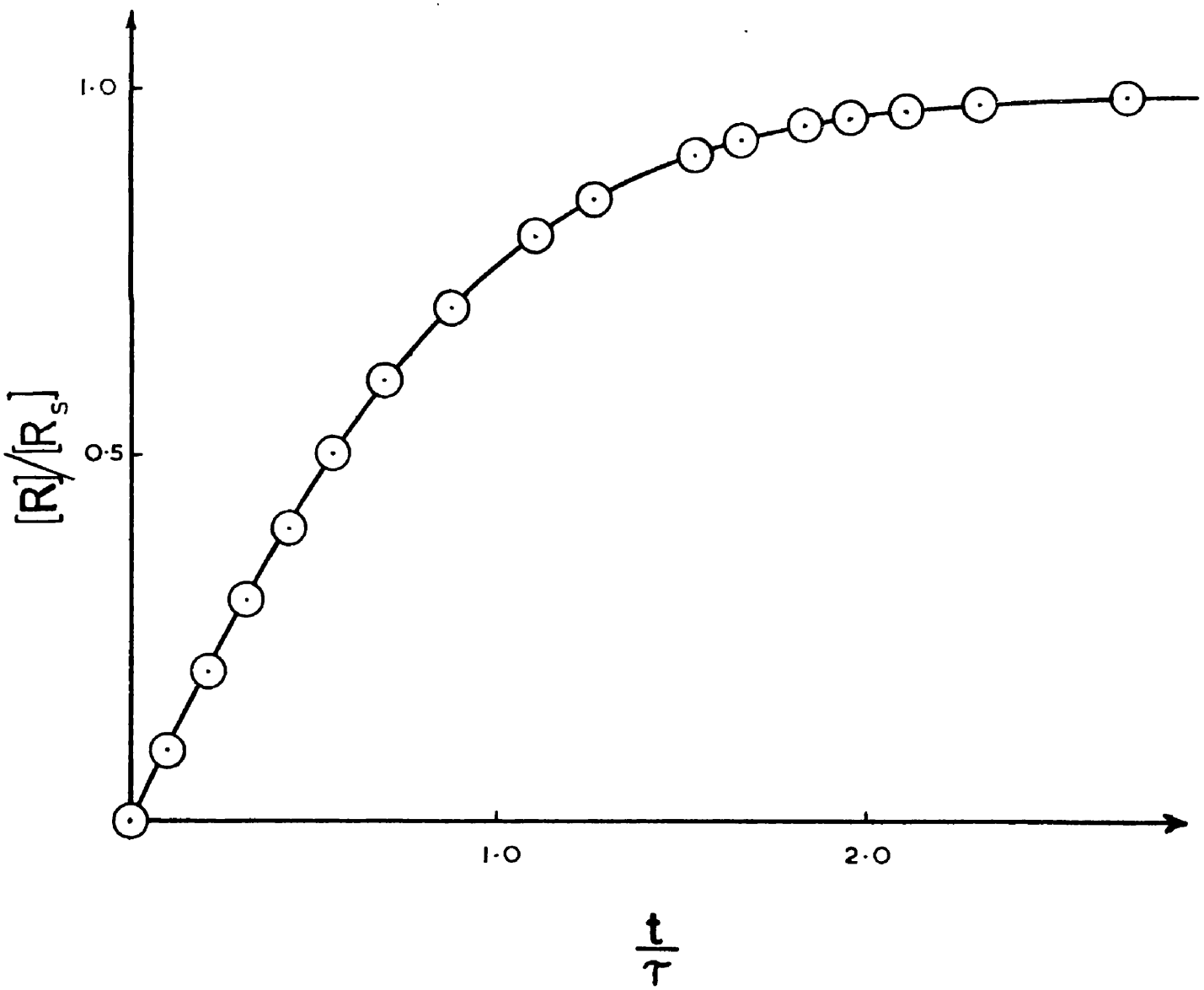
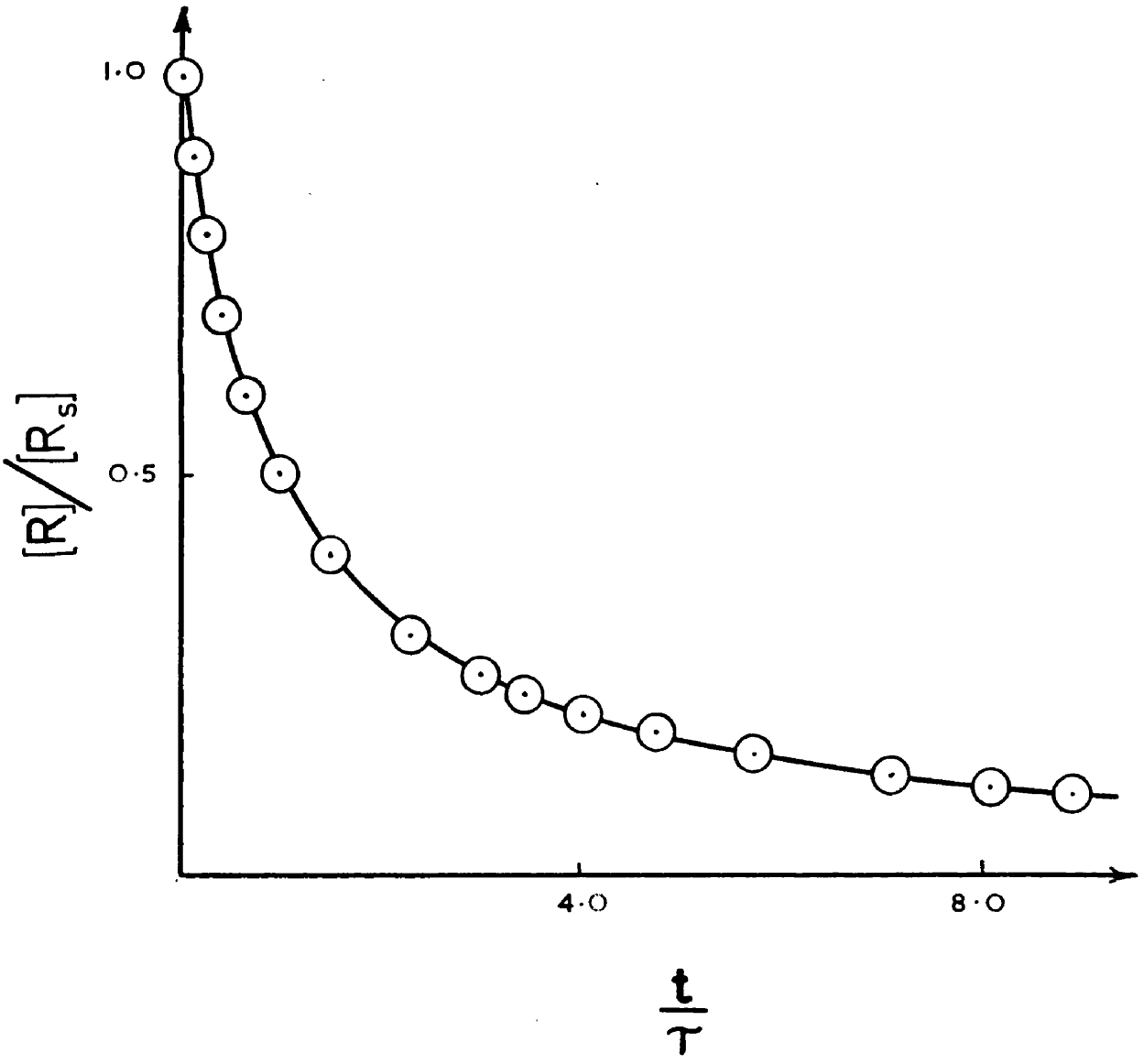


FIG. 26

DECAY OF RADICAL CONCENTRATION.



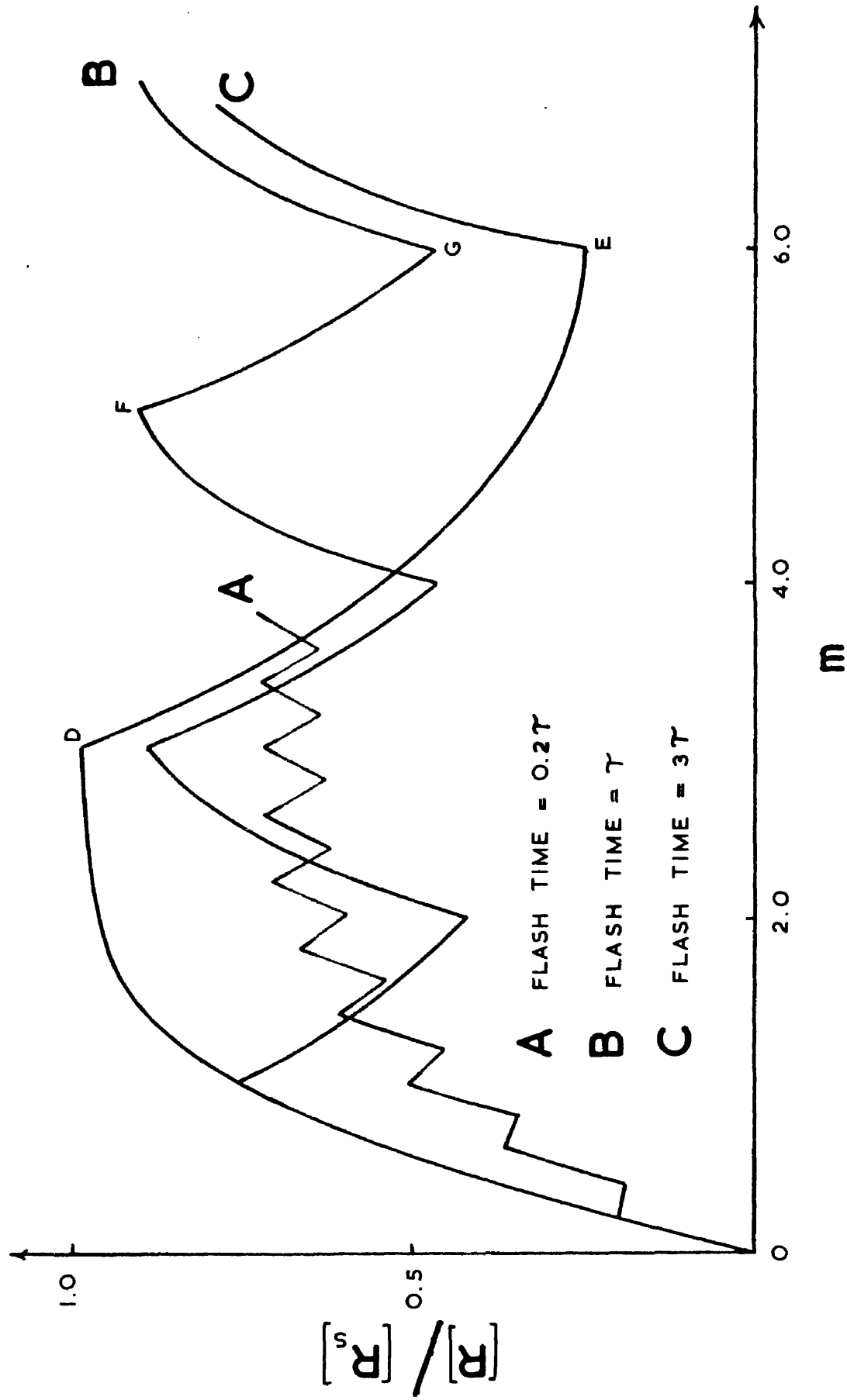

B
C
A
D
F
G
E
A FLASH TIME = 0.2τ
B FLASH TIME = τ
C FLASH TIME = 3τ
1.0
0.5
0
2.0
4.0
6.0
m
[R] / [R_s]

FIG. 27

illumination. The average rate of reaction under these conditions will therefore be 50% of the average rate obtained under steady illumination. When the radical lifetime is longer than the flash time, only a small proportion of the radicals will terminate during the dark period i.e. the reaction will be continuous with virtually no change in rate occurring between the light and dark periods. In this case, the rate of reaction will be 70.7% of the rate at steady illumination.

From Figs.25 and 26, Fig.27 was drawn to show precisely the effect of varying flash times on the radical concentration, the graph being based on equal light and dark periods. For curve C, the flash time, t , is much greater than τ and thus, the radical concentration is virtually equal to $[R_s]$ at the end of the light period. During the dark period, the radical concentration falls along the curve DE to almost zero and this is repeated in each cycle.

Curve B shows the variation in the radical concentration when the flash time is equal to the radical lifetime. During the light period, the radical concentration does not rise to the value of $[R_s]$ and, during the dark period, the decay curve FG does not fall to zero. To reach its pseudo-stationary state, i.e. when $[R_1]$ is a constant, t/τ must be equal to 5.0 .

Curve A shows the variation in the radical concentration when $t = 0.2\tau$. The decrease of the radical concentration due to termination during the dark period is initially smaller than the increase brought about in the succeeding light period. This difference gradually decreases until $t/\tau = 3.8$, when the pseudo-stationary state is reached.

By drawing a series of curves similar to the above for other ratios of t/τ, the ratio of $[R_l]/[R_s]$ was obtained for known values of m. The curve constructed from this data is shown in Fig.28. By substituting the values of this ratio, together with the corresponding values of m, in equation (7.2.21), the ratio of $[R_o]/[R_s]$ was evaluated. Fig.29 shows the curve obtained when $[R_o]/[R_s]$ was plotted against log. m .

Now, from the reaction scheme detailed in section 5.1., the rate of reaction is seen to be proportional to the steady state radical concentration, $[R_s]$. Similarly, for the rotating sector method, the rate of reaction will be proportional to the average radical concentration during the pseudo-stationary state, $[R_o]$. The ratio of $[R_o]/[R_s]$ must therefore be equal to the ratio of the rate of reaction under intermittent illumination to the rate of reaction under steady illumination. Also,

$$\text{log. } m = \text{log. } t - \text{log. } \tau \qquad \ldots(7.2.22)$$

FIG. 28

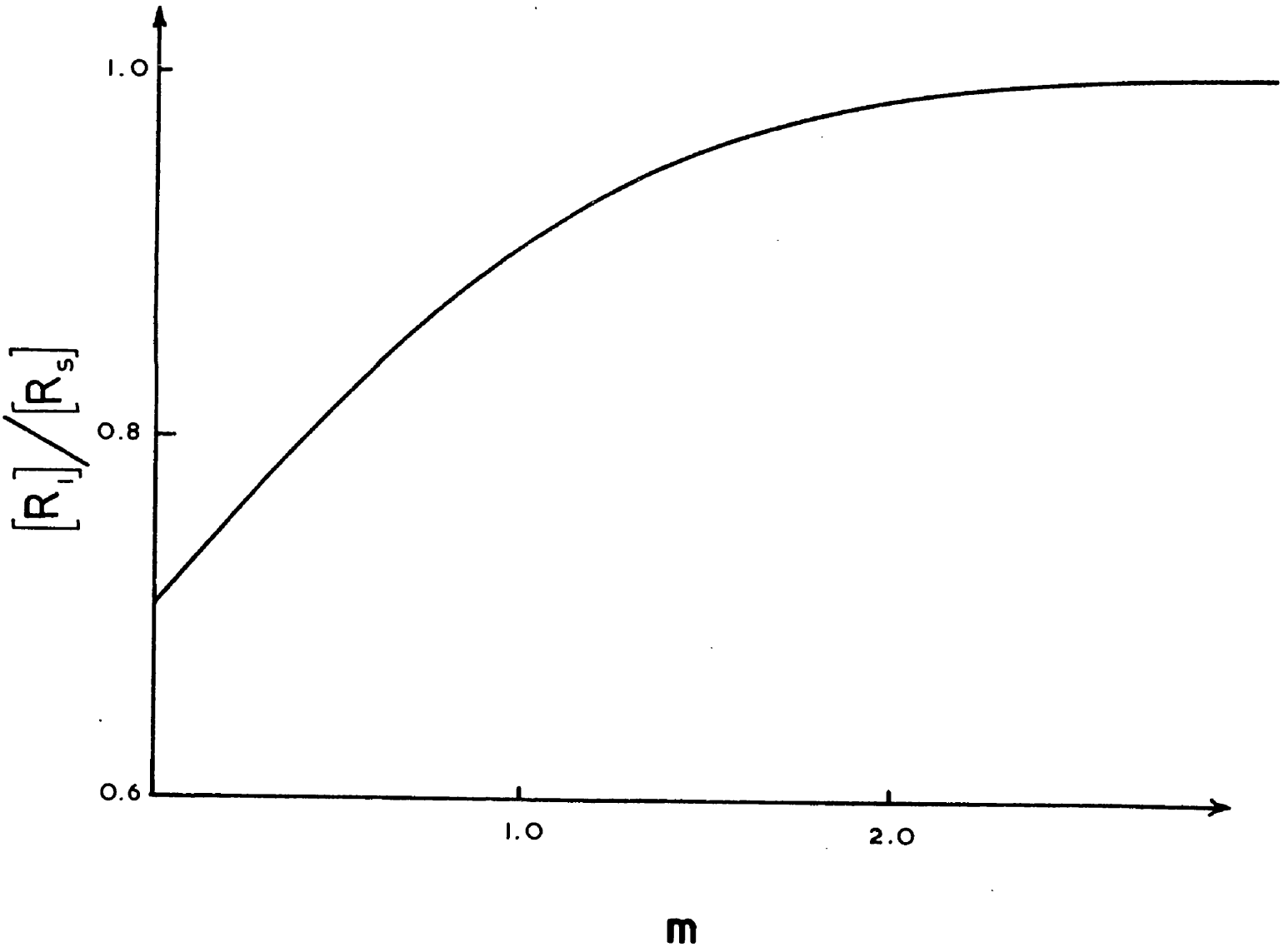


FIG. 29

THEORETICAL CURVE FOR THE MODIFIED ROTATING SECTOR METHOD.

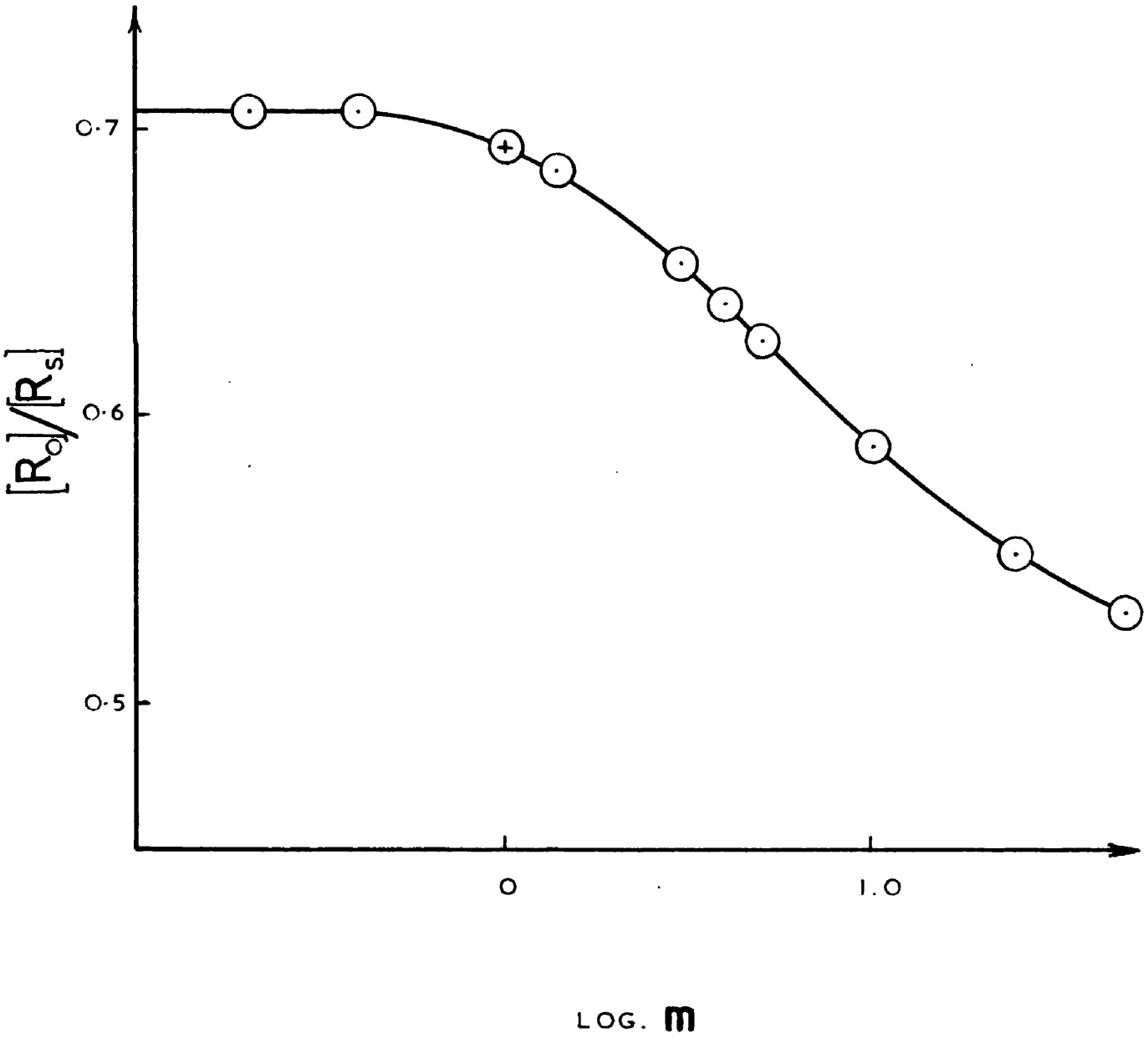
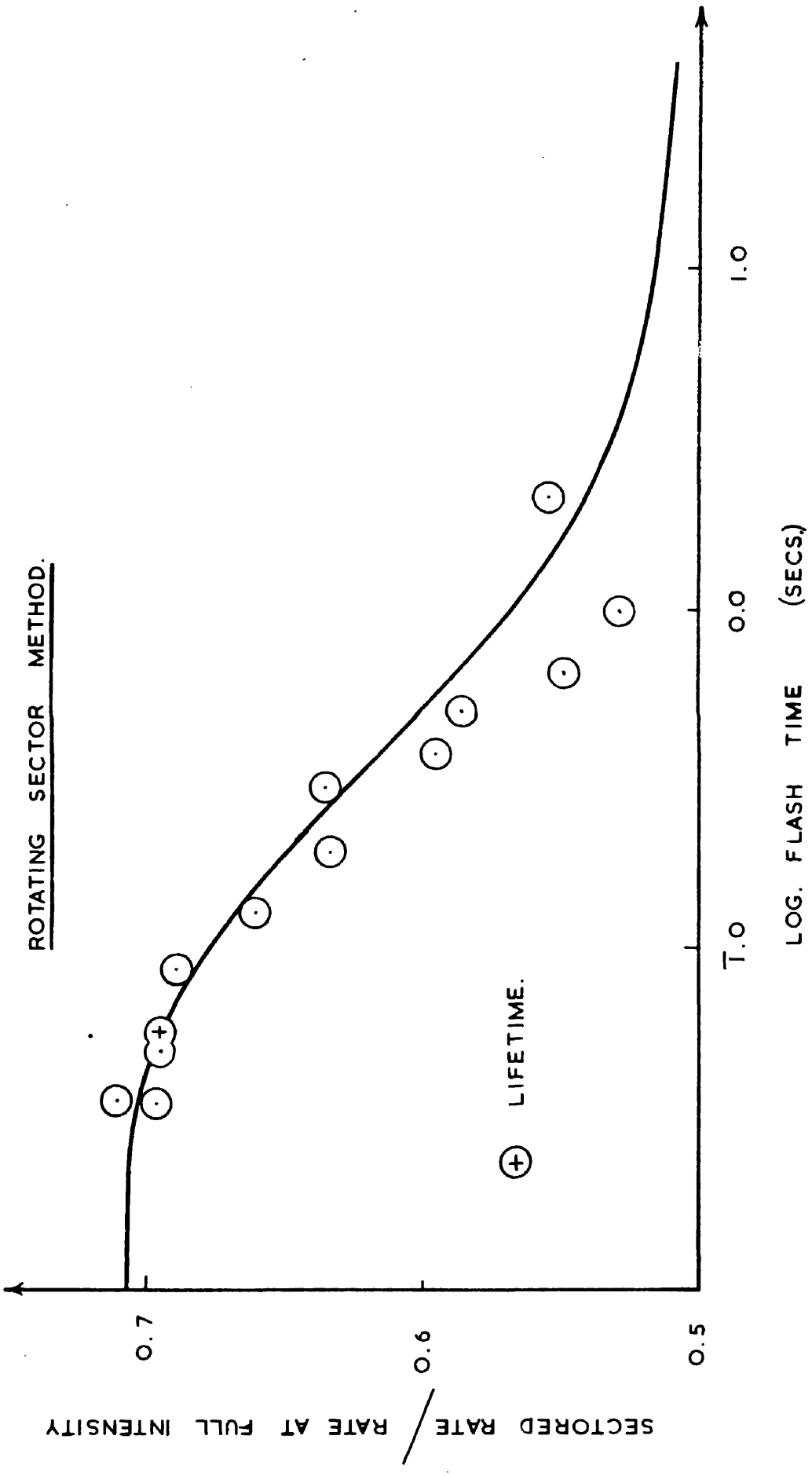


FIG. 30

TYPICAL DETERMINATION OF THE KINETIC CHAIN LIFETIME USING THE MODIFIED ROTATING SECTOR METHOD.



and therefore the plot of the ratio of the sectored rate to the unsectored rate against log.(flash time) must have the same shape as the curve shown in Fig.29.

Also from Fig.29, it is seen that when m = 1, i.e. when the flash time is equal to the lifetime of the kinetic chain, then the ratio of $[R_o]/[R_s]$ is equal to 0.694. When, therefore, the ratio of the sectored rate to the unsectored rate is plotted against log.(flash time), the kinetic chain lifetime will be the time at which the ratio of the two rates is equal to 0.694. Normally, the experimental data was matched to the theoretical curve to obtain a value for the kinetic chain lifetime.

The normal rotating sector method involves the measurement of the reaction rates by following the contraction in volume of the reactants. This means that it is necessary to fill a dilatometer for each point obtained on the experimental curve, if reproducible conditions are to be obtained. Even by doing this, the rate measurements will still be average ones over at least the first five percent conversion.

The modified rotating sector method used by the author[45], eliminates these difficulties and allows a complete determination of the kinetic chain lifetime before 1% conversion has taken place. The method involves the dilatometric measurement of the

initial expansion rate at various flash times. It has been shown in section 4.4. that this is directly proportional to the reaction rate when no heat is flowing into or out of the reaction vessel. Fig.27 shows that the pseudo-stationary state is quickly attained and that this time is well within the period in which adiabatic conditions are maintained in the reaction vessel.

A typical plot of the ratio of the initial expansion rate under intermittent illumination to the unsectored initial expansion rate against log.(flash time) is shown in Fig.30. By matching the experimental points to the theoretical curve, the value of τ, corresponding to the measured reaction rate, was obtained.

7.3. Evaluation of the velocity coefficients for propagation and termination when the intensity exponent is in the range $0.5 < x_i < 1.0$.

It has been shown that, for most free radical initiated polymerisations, the termination reaction is of the second order i.e. the initiator and intensity exponents each have a value of 0.50 .

In the present work, an intensity exponent of 0.70 has been found in the photoinitiated polymerisation of acrylonitrile in bulk, (see section 5.4.5.). This value is almost certainly too high since the initiator exponent at 60°C was found to be 0.56 (section 5.4.3.) and since a value of 0.50 has been reported for the very early stages of the polymerisation[17]. However, the value of 0.70 will be used to illustrate the theory in the following section.

An initiator exponent of 0.70 indicates a mixed termination step involving both first and second order terminations. Using the kinetic analysis derived in sections 5.1. and 7.1. to calculate the velocity coefficients for this reaction would involve some error since equations (5.1.8) and (7.1.18) are based on the assumption of second order termination. To date, only Burnett & Wright[105] have attempted to apply the necessary corrections to a reaction of this type but their theory is not of sufficiently general application. In several cases, where experimental results have indicated a mixed termination reaction, the kinetic treatment has been based on the assumption of second order termination[106-108]. This has led to the following theory being derived by Bengough[109].

Consider the general case represented by the following

kinetic scheme.

$$A + h\nu \rightarrow C\cdot \qquad \text{Rate} = I \qquad \ldots(7.3.1)$$

$$C\cdot + M \rightarrow R_1$$

$$R_1 + M \rightarrow R_n \qquad \text{Rate} = k_2[R][M] \qquad \ldots(7.3.2)$$

$$R_r + R_s \rightarrow \text{Polymer} \qquad \text{Rate} = k_4[R]^2 \qquad \ldots(7.3.3)$$

$$R_r + M \rightarrow \text{Polymer} \qquad \text{Rate} = k_m[R][M] \qquad \ldots(7.3.4)$$

$$R_r + Q \rightarrow \text{Polymer} \qquad \text{Rate} = k_q[R][Q] \qquad \ldots(7.3.5)$$

$$R_r + ? \rightarrow \text{Polymer} \qquad \text{Rate} = k_o[R]\ ? \qquad \ldots(7.3.6)$$

where k_2, k_4, k_m, k_q, and k_o are the velocity coefficients for the propagation, mutual termination, monomer termination, retarder termination, and occlusion termination reactions respectively and Q is a molecule of retarder. The remaining symbols are as defined in section 5.1. Reaction (7.3.6) represents termination of a growing radical by occlusion.

The rate of increase of the concentration of radicals is:

$$d[R]/dt = I - [R]\left\{k_m[M] + k_q[Q] + k_o?\right\} - k_4[R]^2$$

$$\text{or} \quad d[R]/dt = I - [R]X - k_4[R]^2 \qquad \ldots(7.3.7)$$

$$\text{where} \quad X = k_m[M] + k_q[Q] + k_o? \qquad \ldots(7.3.8)$$

At the stationary state, $d[R]/dt = 0$.

$$\text{i.e.} \quad [R_s] = -X/2k_4 + \left\{(X^2 + 4Ik_4)/4k_4^2\right\}^{0.5} \qquad ...(7.3.9)$$

$$\text{or} \quad [R_s] = \alpha - \beta \qquad ...(7.3.10)$$

$$\text{where} \quad \alpha = \left\{(X^2 + 4Ik_4)/4k_4^2\right\}^{0.5} \qquad ...(7.3.11)$$

$$\text{and} \quad \beta = X/2k_4 \qquad ...(7.3.12)$$

Integration of equation (7.3.7) over the time interval from 0 to t will give the value of the radical concentration, $[R]$, at time t:

$$\alpha^{-1}\tanh^{-1}\left\{([R] + \beta)/\alpha\right\} = \alpha^{-1}\tanh^{-1}(\beta/\alpha) + k_4 t \qquad ..(7.3.13)$$

Rearrangement gives:

$$[R] = -\beta + \alpha\tanh\left\{\alpha k_4 t + \tanh^{-1}(\beta/\alpha)\right\} \qquad ...(7.3.14)$$

Now, the rate of polymerisation is given by:

$$-d[M]/dt = k_2 [R][M] \qquad ...(7.3.15)$$

Substituting for $[R]$ in equation (7.3.15) from equation (7.3.14) and then integrating the resultant equation from 0 to t produces:

$$\ln([M_o]/[M]) = k_2\left\{-\beta t + k_4^{-1}\ln(\cosh \alpha k_4 t + \alpha^{-1}\beta \sinh \alpha k_4 t)\right\} \quad \ldots(7.3.16)$$

where $[M_o]$ and $[M]$ are the monomer concentrations initially and at time t respectively.

For $t \ggg (\alpha k_4)^{-1}$, equation (7.3.16) approximates to:

$$\ln([M_o]/[M]) = k_2(\alpha - \beta)t - (k_2/k_4)\ln\left\{2\alpha/(\alpha + \beta)\right\} \quad \ldots(7.3.17)$$

For very low values of conversion of monomer into polymer, it has already been shown, equations (7.1.12) to (7.1.14), that $\ln([M_o]/[M])$ is equal to F, the fractional conversion.

$$\therefore \quad F = k_2(\alpha - \beta)t - (k_2/k_4)\ln\left\{2\alpha/(\alpha + \beta)\right\} \quad ..(7.3.18)$$

This is a straight line which intersects the time axis at t_i where:

$$t_i = \frac{\ln\left\{2\alpha/(\alpha + \beta)\right\}}{k_4(\alpha - \beta)} \quad \ldots(7.3.19)$$

The intercept t_i can be measured using any of the non-stationary state methods.

Further, the intensity exponent, x , is usually determined from the slope of the curve relating log.(rate of reaction) to

log.(intensity of irradiation).

$$\text{i.e.} \qquad x = \frac{d(\ln[R_s])}{d(\ln I)}$$

$$\text{or} \qquad x = I \,/\, 2k_4\alpha(\alpha - \beta) \qquad \ldots(7.3.20)$$

Squaring this and substituting for α and β from equations (7.3.11) and (7.3.12) gives:

$$X^2 = k_4 I(2x - 1)^2/x(1- x) \qquad \ldots(7.3.21)$$

By using the substitution $\alpha = n\beta$, equations (7.3.19) and (7.3.20) can be solved giving:

$$X = \left\{(2x - 1).\ln(1/x)\right\}/(1 - x)t_i \qquad ..(7.3.22)$$

Substituting for X in equation (7.3.21) gives:

$$k_4 = \frac{x\left\{\ln(1/x)\right\}^2}{I.(1 - x).t_i^2} \qquad \ldots(7.3.23)$$

Thus, both X and k_4 can be obtained directly from experimental measurements of the rate of initiation, the intensity exponent, and the intercept t_i.

For the evaluation of k_2, it is necessary to measure the rate of reaction in addition to the above data.

$$k_2 = \text{Rate of reaction}/[R_s][M] \qquad \ldots(7.3.24)$$

Substituting for $[R_s]$ from equation (7.3.9) and again for X from equation (7.3.21), equation (7.3.24) becomes:

$$k_2 = (\text{rate})(xk_4)^{0.5}/[M]\left\{(1-x)I\right\}^{0.5} \qquad \ldots(7.3.25)$$

Thus, from equations (7.3.25) and (7.3.23), the true values of the velocity coefficients for propagation and termination may be obtained.

Now, let k_4' be the calculated value of the velocity coefficient for termination when exclusive second order termination is assumed.

$$\text{i.e.} \quad k_4' = (\ln 2)^2/It_i^2 \qquad \ldots(7.3.26)$$

The correct value of k_4 is given in equation (7.3.23)

$$\therefore \quad \frac{k_4}{k_4'} = \frac{x\left\{\ln(1/x)\right\}^2}{(1-x)(\ln 2)^2} \qquad \ldots(7.3.27)$$

Correction factors for various values of the intensity

FIG. 31

CORRECTION FACTORS TO ALLOW FOR HIGH INTENSITY EXPONENTS.

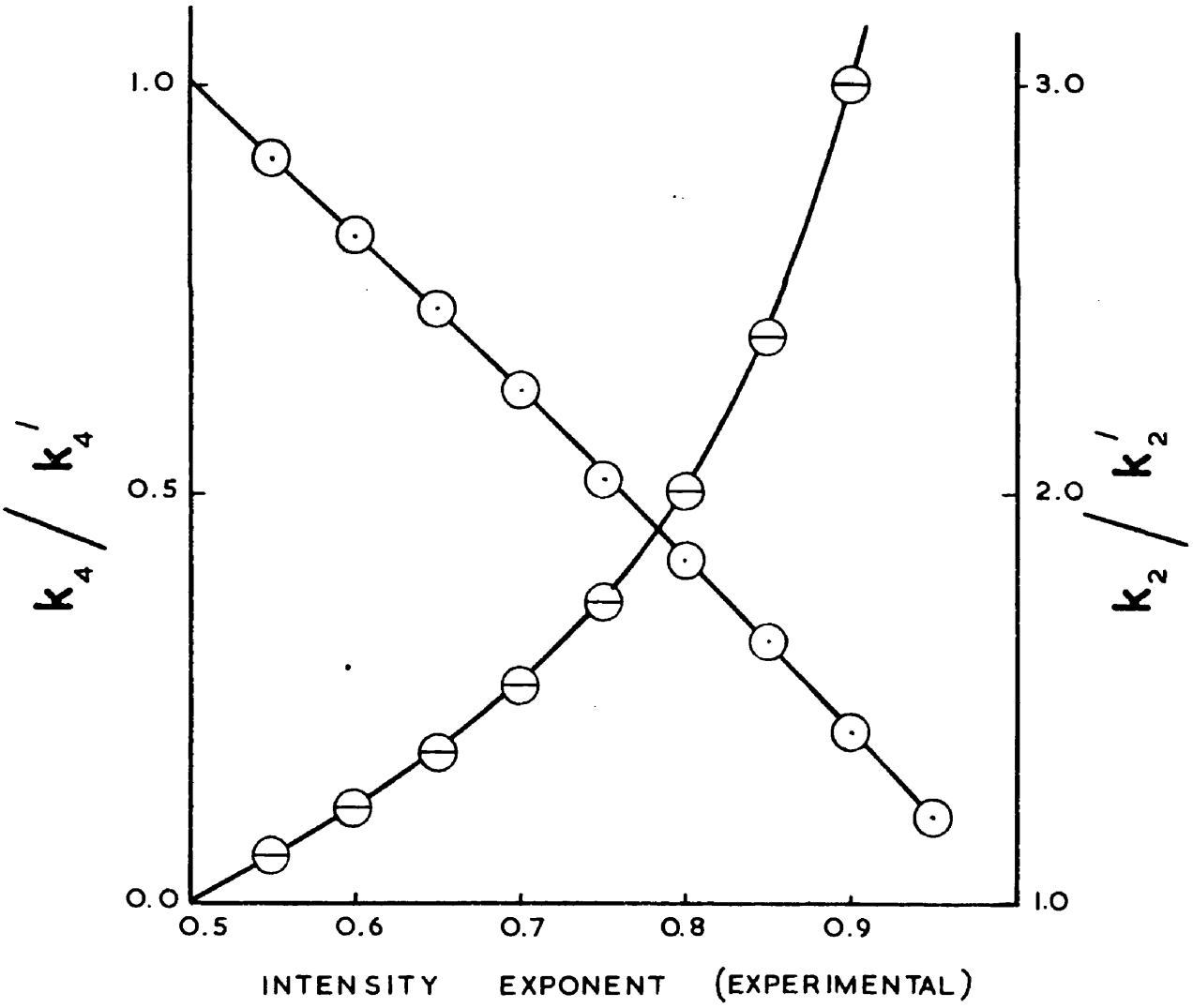
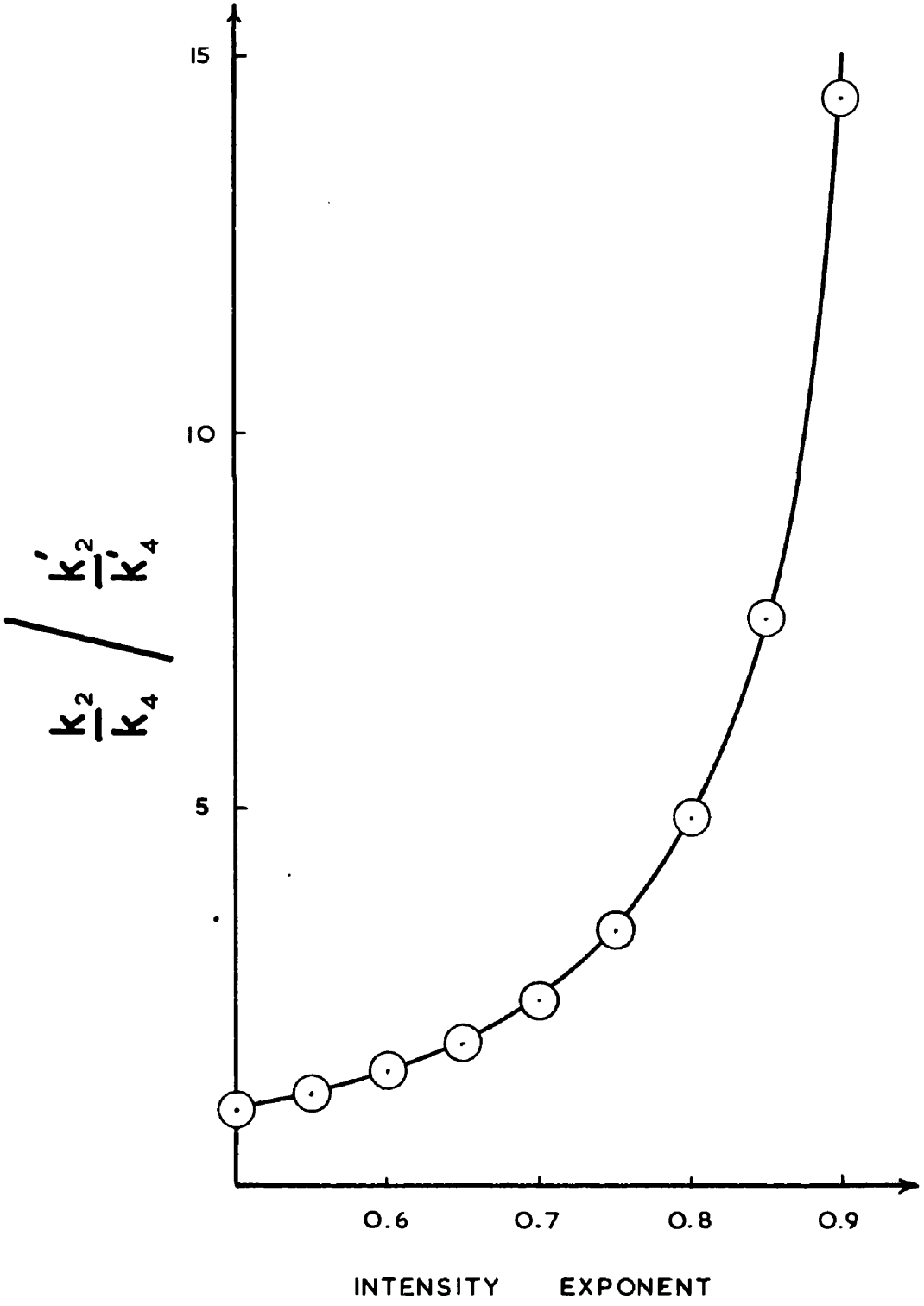


FIG. 32

CORRECTION FACTORS TO ALLOW FOR HIGH INTENSITY EXPONENTS.



exponent are given in Fig.31. It can be seen from this that, even for an intensity exponent of 0.75, the correction is slightly less than a factor of two. This error is not excessively large for this type of work. The 20% error involved with intensity exponents of up to 0.6 will be within the normal scatter of experimental results.

The correction factor for the velocity coefficient of propagation is similarly found:

$$k_2/k_2' = x / (1 - x)^{0.5} \qquad \ldots(7.3.28)$$

where k_2' is the value calculated assuming exclusive second order termination. The correction factors for k_2 are also shown in Fig.31. It will be noticed that, although the percentage errors in k_2 and k_4 have similar magnitudes, they are of opposite sign.

The correction factor for the ratio of k_2/k_4 is shown in Fig.32 and it is apparent that this ratio is affected to a much greater extent than either of the two individual velocity coefficients.

7.4. Results.

7.4.1. Applicability of the non-stationary state methods of determining the kinetic chain lifetime.

It was found that the modified rotating sector method[45] could only be used for reaction mixtures containing 40% acrylonitrile (v/v) or less, since the kinetic chain lifetime in these mixtures was below 0.3 secs. For reaction mixtures containing a higher percentage of acrylonitrile, the lifetime was found to be greater than 0.3 secs. and cooling effects completely precluded the use of the modified rotating sector method. For lifetimes of this order, the direct dilatometric method was used[39].

An attempt was also made to apply this direct method to reaction mixtures containing less than 40% acrylonitrile but an extremely wide scatter of experimental results was obtained and no reliable values of the velocity coefficients could be found.

7.4.2. Evaluation of the ratio of k_2/k_4.

The values of this ratio were obtained from equation (7.1.18)

and the following table gives the average values obtained for the stated reaction mixtures.

Table 12. Evaluation of the ratio of k_2/k_4 by the dilatometric and the modified rotating sector techniques (at 25°C).

Monomer concentration (mol./l.)	k_2/k_4
15.10	6.92×10^{-6}
14.31	7.77×10^{-6}
12.05	2.35×10^{-5}
9.05	1.54×10^{-5}
6.03	2.50×10^{-6}
4.54	2.72×10^{-6}
3.02	1.13×10^{-6}

7.4.3. Evaluation of the ratio of $k_2/k_4^{0.5}$.

By using equation (5.1.8), individual values of this ratio were derived. The arithmetical average of the values obtained (i.e. those quoted in Table 13) cannot be directly correlated to the values given above for the ratio of k_2/k_4. The data in

Table 13 has been presented to allow comparison with published work where the results have frequently been stated in this form.

Table 13. Evaluation of the ratio of $k_2/k_4^{0.5}$ using equation (5.1.8).

Monomer concentration. (mol./l.)	$k_2/k_4^{0.5}$
15.10	4.42×10^{-2}
14.31	5.21×10^{-2}
12.05	8.67×10^{-2}
9.05	9.40×10^{-2}
6.03	4.75×10^{-2}
4.54	7.00×10^{-2}
3.02	6.19×10^{-2}

7.4.4. Evaluation of the velocity coefficients for propagation and termination.

The data given in Table 14 below once again consists of the average values obtained at the quoted monomer concentrations. The constants were all determined at 25°C and the kinetic scheme defined by equations (7.1.18) and (5.1.8) has been assumed to

hold over the complete range of monomer concentrations.

Table 14. Average values of the velocity coefficients for propagation and termination obtained by the dilatometric and modified rotating sector techniques, at 25°C.

[M]	k_2	k_4
15.10	3.01×10^2	4.78×10^7
14.31	3.67×10^2	5.01×10^7
12.05	3.20×10^2	1.36×10^7
9.05	5.80×10^2	3.82×10^7
6.03	9.02×10^2	3.60×10^8
4,54	2.26×10^3	1.23×10^9
3.02	3.39×10^3	3.00×10^9

where [M] is expressed as mol./l. and k_2 and k_4 are expressed as $mol.^{-1} l.sec.^{-1}$.

A heat of polymerisation of 17.5 Kcal./mol.[61] has been used in the above calculations, and the rate of initiation has been taken as 6.91×10^{-8} $mol.l.^{-1}sec.^{-1}$ (see section 6.3.5.).

7.4.5. Evaluation of the velocity cefficients using the experimentally determined value for the heat of polymerisation.

From section 4.2.3., the heat of polymerisation as determined dilatometrically in an 80% DMF - 20% AN reaction mixture is 23.0 Kcal./mol. . This gives the fractional contraction for complete reaction as 7.81×10^{-2} compared to the value of 4.36×10^{-2} used above.

Table 15. Values of the velocity coefficients obtained assuming a heat of polymerisation of 23.0 Kcal./mol. .

[M]	$k_2/k_4^{0.5}$	k_2/k_4	k_2	k_4
3.02	3.45×10^{-2}	6.35×10^{-7}	1.88×10^{3}	2.98×10^{9}

This correction therefore reduces the value of k_2 by a factor of two and does not affect k_4.

In section 4.3., it is stated that the values for the heat of polymerisation obtained in homogeneous mixtures were quite consistent whilst those obtained in heterogeneous mixtures were widely scattered. It may be that the value of 23.0 Kcal./mol.

is specific for polymerisation in the homogeneous region and that a lower value (around 17.5 Kcal./mol.) would be obtained in the heterogeneous region.

In spite of the disparity between these results, it was decided that no advantage would be gained in applying the calorimetric methods of Tong & Kenyon[61] to evaluate the heat of polymerisation for each of the reaction mixtures since the resultant variation in k_2 and k_4 would not alter the main trend of the results.

7.4.6. Evaluation of the velocity coefficients using the experimentally determined value for the intensity exponent.

From section 5.4.5., it is seen that the intensity exponent in the bulk polymerisation was found to be 0.70. As has been stated in section 5.5.3., this value of the intensity exponent is believed to be too high but it will be used here to show the effect on the velocity coefficients if mixed order termination does indeed occur. From Fig. 31, the correction factors for k_2 and k_4 are 1.527 and 0.622 respectively. This gives:

$$k_2 = 4.59 \times 10^2$$

$$k_4 = 2.98 \times 10^7$$

This correction therefore makes a difference of less than a factor of two in the final values of k_2 and k_4 and, since this is within the limits of experimental reproducibility, the correction has not been applied to the remainder of the results.

7.5. Discussion.

7.5.1. Techniques used for the determination of the kinetic chain lifetime.

In the dilatometric method[39], the main difficulties encountered were the relatively short period (~ 20 secs.) in which adiabatic conditions were maintained in the system and the accuracy of extrapolation. When the kinetic chain lifetime was of the order of 1 sec., these difficulties introduced an error of about 20 - 30 % to the determination. This is quite reasonable for this type of work. At lifetimes of less than 0.5 secs., however, the errors introduced were considerable and, due to the difficulty of extrapolation, the results obtained were valueless.

To overcome these drawbacks, the modified rotating sector method[45] was introduced. No time axis intercept was required

in this technique - only the simple measurement of an initial expansion rate was necessary. This could be accurately performed and thus the errors involved in this method were small. It was also found that this method gave a high degree of reproducibility.

The one major defect of the modified rotating sector method was that, at long flash times, the cooling rate of the system became appreciable and the expansion rates obtained could no longer be correlated to the absolute reaction rate.

Thus, the dilatometric method and the modified rotating sector method are complementary and can be used to determine kinetic chain lifetimes of up to 2.0 secs..

7.5.2. Interpretation of the above results.

As was stated in the introduction, the discussion here will be limited to a consideration of the individual values obtained for each reaction mixture. The significance of the relation between these values will be discussed in chapter 9.

Table 13 gives values of the ratios obtained for $k_2/k_4^{0.5}$. The variation over the entire monomer concentration range involves a factor of just over two. Since the variation of the ratio over each series of experiments at any one monomer

concentration did not exceed 10%, the spread of the final results must be considered significant.

The ratio of $k_2/k_4^{0.5}$ increases initially as the concentration of monomer decreases until a concentration of 6.03 mol./l. is reached. The value obtained here is indeterminate and does not seem to fit in with the general trend of results. In the homogeneous region, the value of the ratio decreases with decreasing monomer concentration.

In the evaluation of the ratio of k_2/k_4 at any one monomer concentration, the maximum spread round the average value was $\pm$ 50%. Since in most cases, the error was much less than this, the data in Table 12 must be taken as showing an initial increase in the value of k_2/k_4 as the monomer concentration decreases. At a monomer concentration of 6.03 mol./l., an abrupt change is apparent, the value of the ratio decreasing by a factor of six from the previous result. In the homogeneous region, the ratio of k_2/k_4 may decrease further but, due to the difference between the results (approximately 58%), it is not possible to draw any definite conclusions on this matter. Over this range, however, it is obvious that no increase occurs in the value of the ratio of k_2/k_4.

It is apparent from the above discussion that the absolute

values of the velocity coefficients (Table 14) can be taken as being constant over the heterogeneous range. A sudden increase in the values of both k_2 and k_4 occurs at a monomer concentration of 6.03 mol./l. and the values again become virtually constant when the monomer concentration is 4.54 mol./l. or less. The increase in the values of k_2 and k_4 observed between the monomer concentrations of 4.54 and 3.02 mol./l. cannot be regarded as significant.

It is seen, therefore, that the correction applied in section 7.4.5. would make no difference to the variation in k_4 although it would minimise the range of values obtained for k_2. The correction applied in section 7.4.6. to take account of the possible high intensity exponent for the bulk polymerisation, would emphasise the wide range of values obtained for k_4 and would also tend to minimise the range obtained for k_2.

However, it must be concluded that large variations in the values of k_2 and k_4 are obtained over the range of monomer concentration studied in this work. The variation in the velocity coefficient for termination is approximately ten times the variation observed in the values of the velocity coefficient for propagation.

CHAPTER 8.

Determination of the overall energy of activation for the polymerisation of acrylonitrile and the velocity coefficient for transfer with dimethyl formamide and with bromotrichloromethane.

8.1. Energy of activation.

It is generally accepted that the velocity coefficient of a reaction (k) may be related to the energy of activation by the equation:

$$k = A.\, e^{-\frac{E}{RT}} \qquad \ldots(8.1.1)$$

where A, the frequency factor, represents the total frequency of

encounters between the reactant species; E is the energy of activation for the reaction; T is the temperature (in degrees absolute) at which the reaction occurs; and R is the molar gas constant.

It has been shown (section 5.1.) that the rate of polymerisation may be written:

$$\text{Rate} = k_2 [R_s] [M] \qquad \ldots(8.1.2)$$

$$= \frac{k_2 k_i^{0.5}}{k_4^{0.5}} [C]^{0.5} [M] \qquad \ldots(8.1.3)$$

let $$k_o = \frac{k_2 k_i^{0.5}}{k_4^{0.5}} \qquad \ldots(8.1.4)$$

then equation (8.1.3) may be written:

$$\text{Rate} = k_o [C]^{0.5} [M] \qquad \ldots(8.1.5)$$

and $$k_o = A. e^{-\frac{E_o}{RT}} \qquad \ldots(8.1.6)$$

where E_o will be the overall energy of activation and will have the value:

$$E_o = E_2 + \tfrac{1}{2}E_i - \tfrac{1}{2}E_4 \qquad \ldots(8.1.7)$$

where E_2 , E_4 , and E_i are the energies of activation for the propagation, termination, and initiation reactions respectively.

In the present work, only the overall energy of activation has been evaluated, this being carried out over a wide range of monomer concentrations. There was a two fold reason for doing this series of experiments: to find the variation, if any, in E_o as the monomer concentration was varied from 3.22 mol/l. to 14.39 mol/l. and, secondly, to confirm the low values obtained for the dark rate in the photoinitiated polymerisation at 25°C.

To find the absolute value of the overall energy of activation, equation (8.1.6) has to be rewritten in the form:

$$\ln k_o = - \frac{E_o}{R\,T} + \ln A \qquad \ldots(8.1.8)$$

Since [C] and [M] are virtually constant over the first few percent reaction, then the rate of polymerisation is directly proportional to k_o i.e.

$$\log \text{Rate} = - \frac{E_o}{2.303RT} + \log A + \log[M] + 0.5 \log[C] \qquad \ldots(8.1.9)$$

or

$$\log \text{Rate} = -\frac{E_o}{2.303RT} + \log K$$

where K is a constant.

Thus, the value of E_o was calculated from the slope of the curve obtained by plotting log. Rate against 1/T.

For reactions taking place in a heterogeneous medium, the overall energy of activation was calculated from instantaneous values of the rate of reaction when 1%, 2%, and 3%, of the monomer had been converted to polymer. The value quoted for each monomer concentration in Table 16 is the average of these three determinations.

8.2. Velocity coefficients for chain transfer.

The chain transfer reactions considered are:

(i) Transfer to monomer (velocity coefficient k_m):

$$R + M \rightarrow \text{Polymer} + M\cdot \qquad \ldots(8.2.1)$$

(ii) Transfer to a transfer agent, S, (velocity coefficient k_s):

$$R + S \rightarrow \text{Polymer} + S\cdot \qquad \ldots(8.2.2)$$

The propagation and termination steps are as described in section 5.1., second order termination again being assumed.

Let the degree of polymerisation be $\overline{DP}$, then:

$$\overline{DP} = \frac{\text{Rate of chain growth}}{\text{Rate of chain termination}} \qquad \ldots(8.2.3)$$

i.e. $$\overline{DP} = \frac{k_2[R][M]}{k_4[R]^2 + k_m[R][M] + k_s[R][S]} \qquad \ldots(8.2.4)$$

or $$\frac{1}{\overline{DP}} = \frac{k_4[R]}{k_2[M]} + \frac{k_m}{k_2} + \frac{k_s[S]}{k_2[M]} \qquad \ldots(8.2.5)$$

If $\overline{DP}_o$ is the degree of polymerisation obtained when S = 0,

$$\overline{DPo} = \frac{k_2[R][M]}{k_4[R]^2 + k_m[R][M]} \qquad \ldots(8.2.6)$$

or $$\frac{1}{\overline{DP}_o} = \frac{k_4[R]}{k_2[M]} + \frac{k_m}{k_2} \qquad \ldots(8.2.7)$$

Equation (8.2.5) may therefore be written:

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_o} + \frac{k_s[S]}{k_2[M]} \qquad \ldots(8.2.8)$$

This theory was first suggested by Mayo[48] and the plot of

$1/\overline{DP}$ against [S]/[M]is commonly called the Mayo plot. From the slope of this curve, the ratio of k_s/k_2 is obtained.

This ratio has been evaluated for the transfer reactions of DMF and bromotrichloromethane with acrylonitrile. The former reaction used AIBN as the initiator whilst in the latter reaction, the BTCM acted as the photoinitiator.

8.2.1. Determination of the degree of polymerisation.

The degree of polymerisation was estimated by a viscometric technique in each case.

In this, the viscosity of a polymer solution (η_m) is measured and compared to the viscosity of the pure solvent (η_o). This ratio is termed the relative viscosity:

$$\eta_r = \frac{\eta_m}{\eta_o} \qquad \ldots(8.2.9)$$

The incremental viscosity due to the polymeric solute is termed the specific viscosity (η_{sp}) i.e.

$$\eta_{sp} = \frac{\eta_m - \eta_o}{\eta_o} \qquad \ldots(8.2.10)$$

or

$$\eta_{sp} = \eta_r - 1 \qquad \ldots(8.2.11)$$

If c is the concentration of polymer in the solvent, normally expressed as g./100 ml., the ratio of η_{sp}/c is a measure of the capacity of the polymer to increase the relative viscosity. Thus, the limiting value of this ratio as c tends to zero will give a quantity characteristic of the given polymer molecule in a specific solvent i.e.

$$\lim_{c \to 0} \frac{\eta_{sp}}{c} = [\eta] \qquad \ldots(8.2.12)$$

where $[\eta]$ is the intrinsic viscosity.

The normal method of obtaining the intrinsic viscosity is to plot the ratio of η_{sp}/c against c and extrapolate to zero concentration, the graph usually being linear where η_r is less than 2.

This method was found to give reasonably satisfactory results but the extrapolations were not always completely reproducible. It was therefore decided to apply a mathematical method of extrapolation. The formula suggested by Schulz & Sing[47] gave excellent reproducibility between different determinations on the same polymer sample. The formula is:

$$\eta = \frac{\eta_{sp}}{1 + 0.28\,\eta_{sp}} \qquad \ldots(8.2.13)$$

where η is the ideal specific viscosity and is related to the intrinsic viscosity by the relation:

$$\eta = c[\eta] \qquad \ldots(8.2.14)$$

Equations (8.2.13) and (8.2.14) are valid for solutions of different polymers in a variety of solvents provided the specific viscosity is less than 1.5 .

A relation between the viscosity of a polymer solution and the molecular weight of the polymer was first suggested by Staudinger et al[110,111]. A modification of his equation, proposed by Houwink[112], is now used:

$$[\eta] = K \cdot \bar{M}_n^{\alpha} \qquad \ldots(8.2.15)$$

where K and α are constants and $\bar{M}_n$ is the number average weight.

Various values have been suggested for K and α.[20,62,113-119] All have been subjected to some criticism and the values which have been used here to calculate the molecular weight are due to Onyon,[62] namely:

$$[\eta] = 3.92 \times 10^{-4} \bar{M}_n^{0.75} \qquad \ldots(8.2.16)$$

These values are close to those found by Cleland & Stockmeyer[117]

and have been confirmed by Peebles[119].

The value of the degree of polymerisation was then calculated from the molecular weight which was found by applying the above equation (8.2.16).

8.3. Results.

8.3.1. Evaluation of the overall energy of activation

This was performed over a wide range of monomer concentrations - from 3.22 mol/l to 14.39 mol/l, the temperature range being from 50°C to 70°C.

Over the lower ranges of monomer concentration, an accurately linear plot of log.(Rate) against 1/T was obtained but, at higher monomer concentrations, there was a wider scatter of results due mainly to the difficulty of obtaining the values of the instantaneous rates. Figs.33 and 34 show the graphs obtained at monomer concentrations of 2.88 mol./l. and 11.51 mol./l. respectively.

FIG. 33

TYPICAL DETERMINATION OF THE ENERGY OF ACTIVATION IN THE SOLUTION POLYMERISATION OF ACRYLONITRILE.

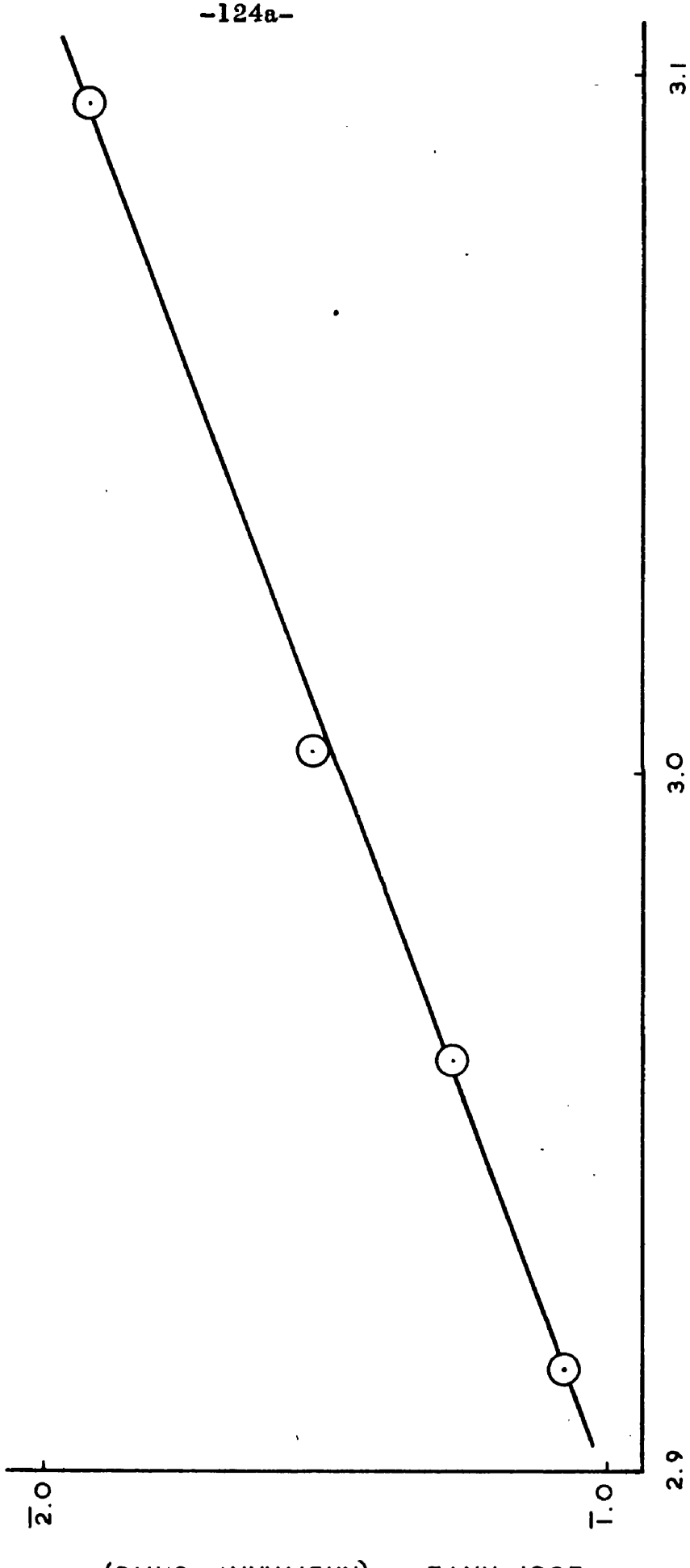


FIG. 34

TYPICAL DETERMINATION OF THE ENERGY OF ACTIVATION IN THE HETEROGENEOUS POLYMERISATION OF ACRYLONITRILE.

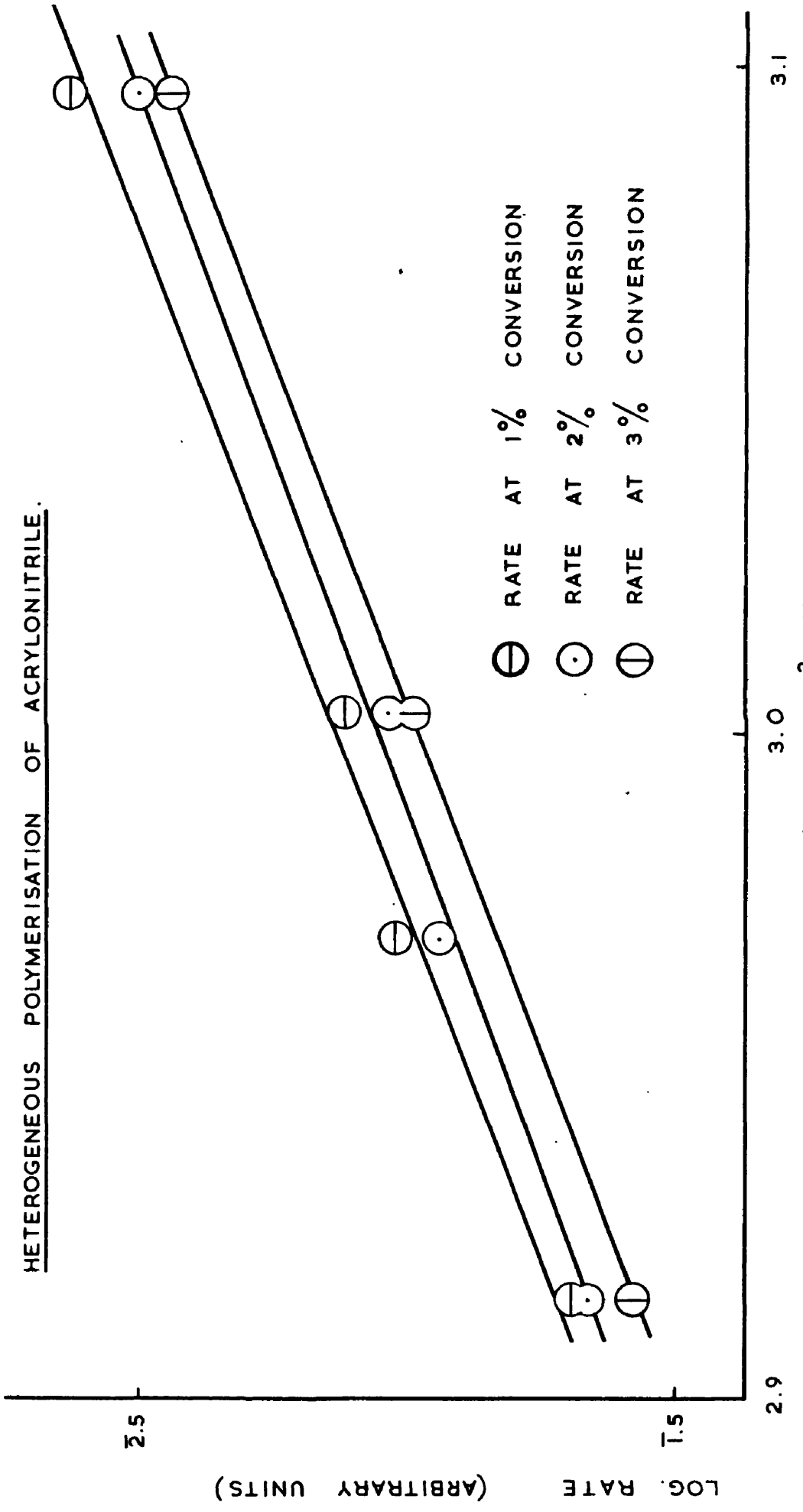


Table 16. Evaluation of the overall energy of activation in the AIBN initiated polymerisation of acrylonitrile over the temperature range from 50°C to 70°C.

$[M]$ (mol./l.)	E (Kcal./mol.)
Bulk AN	26.7
12.82	24.7
11.51	21.7
10.08	22.5
8.63	22.5
7.19	21.0
5.75	21.4
4.31	21.7
2.88	21.4
1.44	22.4

The above table was constructed using instantaneous values for the rate of reaction. It was decided to evaluate the overall energy of activation for the bulk polymerisation of acrylonitrile by taking average rates over the first 30 minutes of reaction. This gave a value of 34.3 Kcal./mol. for E_o.

8.3.2 Dark rate.

Using the data in Table 16 and assuming that the frequency factor remained constant over the range from 25°C to 70°C, the following equation was obtained.

$$\frac{\text{Rate of reaction at } 70^{\circ}C}{\text{Rate of reaction at } 25^{\circ}C} = e^{4.80} \qquad \ldots(8.3.1)$$

The average value of 21.8 Kcal./mol. for E_o was used to derive the above equation.

By applying equation (8.3.1), it was shown that the dark rate in the photoinitiated polymerisations at 25°C was less than 1% of the reaction rate in all cases. This confirmed the rough results which had been obtained by direct observation of the reaction mixtures at 25°C.

8.3.3. Evaluation of the chain transfer coefficients.

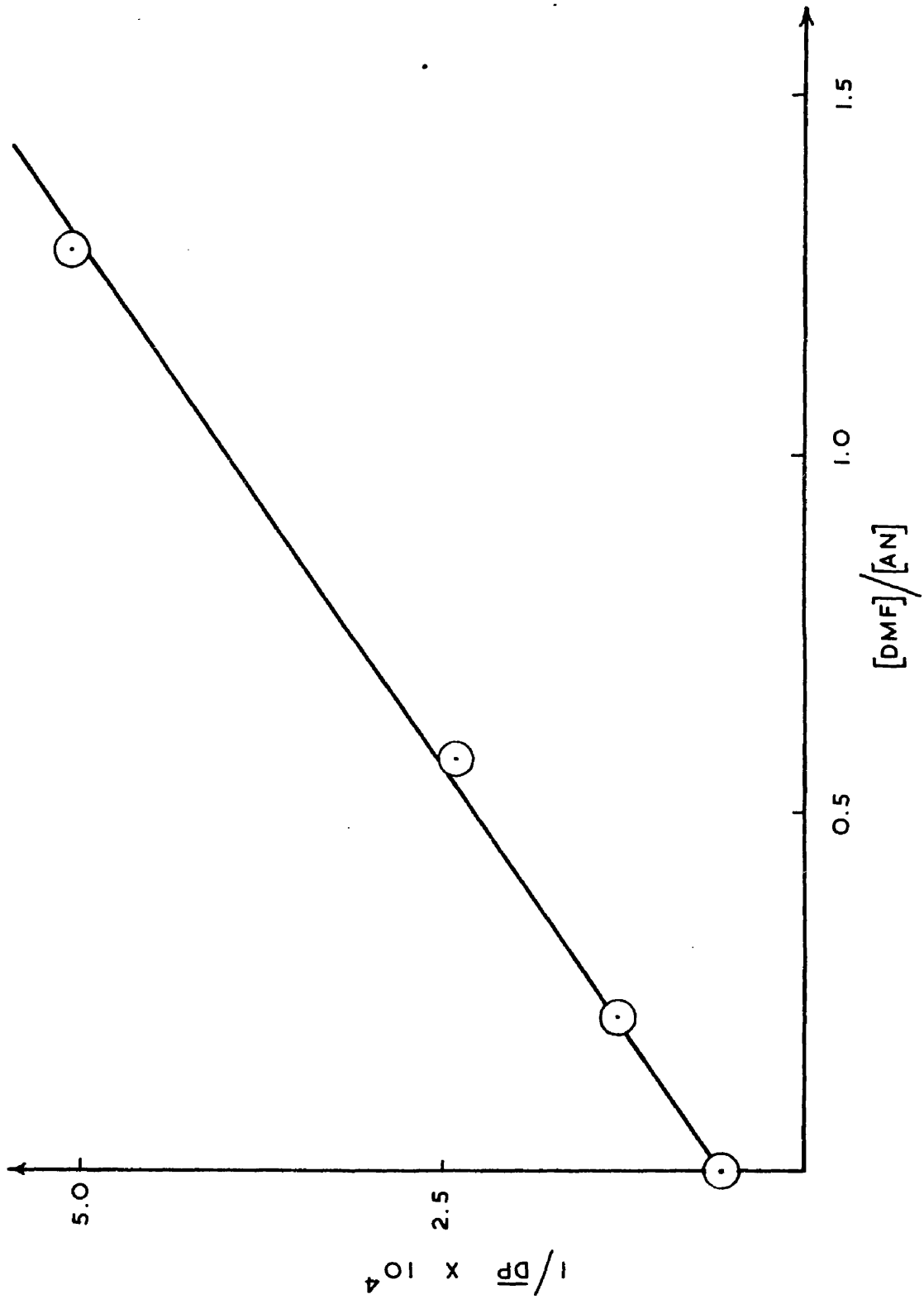
(a) Dimethylformamide and acrylonitrile:

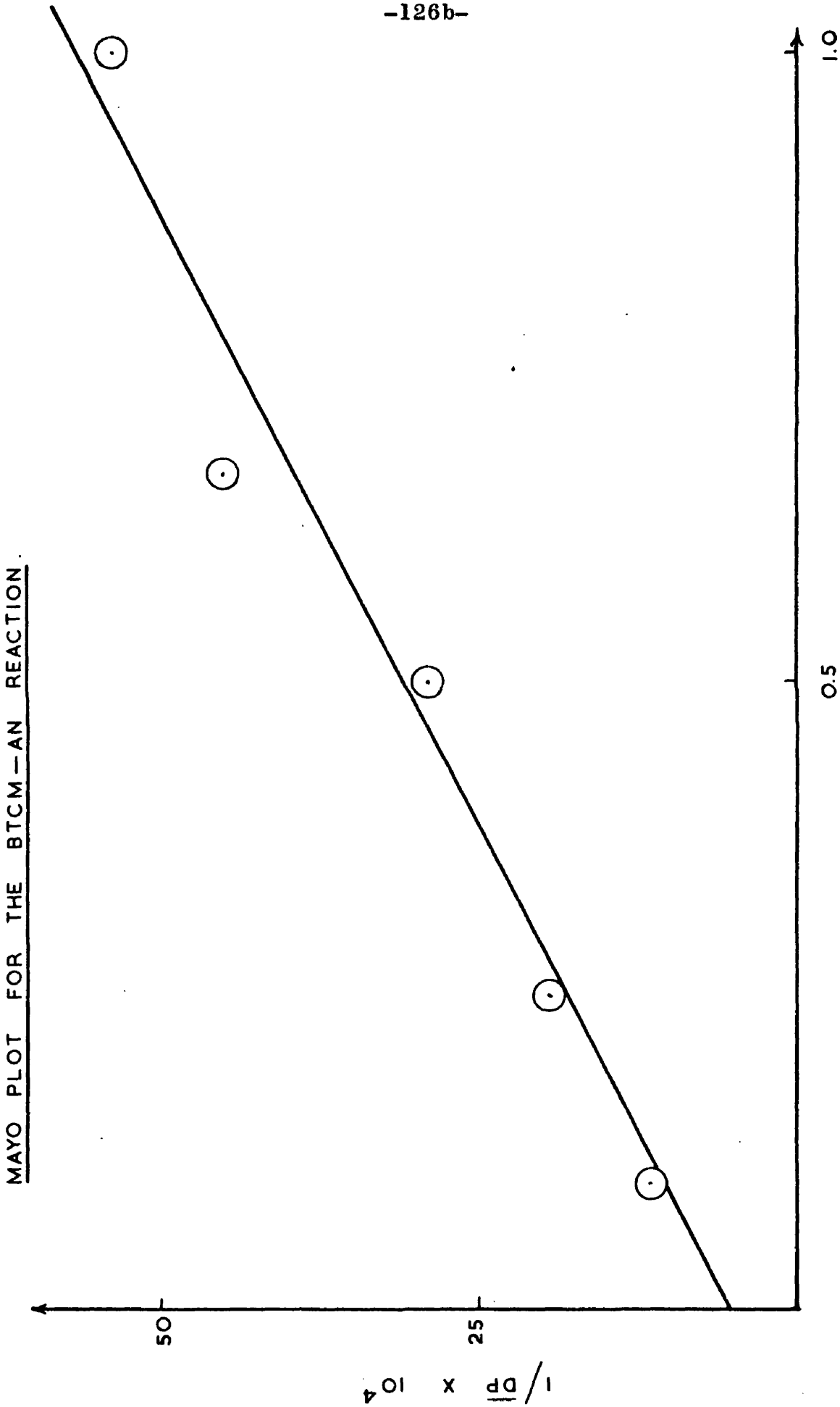
The ratio of k_s/k_2 was found at 25° C using 1.0×10^{-3} mol./l. of AIBN as photosensitiser. The determination was performed only with reaction mixtures which gave heterogeneous polymerisation.

The Mayo plot is shown in Fig. 35.

FIG. 35

MAYO PLOT FOR THE DMF—AN REACTION.





MAYO PLOT FOR THE BTCM—AN REACTION.

FIG. 36

(b) Bromotrichloromethane and acrylonitrile:

The molar ratio of BTCM to AN was varied from 0.10 to 1.0, all the polymerisations being heterogeneous. The Mayo plot for this system is shown in Fig. 36.

Attempts were made to determine the value of the ratio of k_s/k_2 at higher molar ratios of BTCM /AN but the molecular weights of the products were too low to be determined viscometrically The products were insoluble in the solvents commonly used for cryoscopic determinations and their molecular weights were therefore not obtained.

Table 17. Values of the ratio of k_s/k_2 in the polymerisation of acrylonitrile at 25°C

Transfer agent.	k_s/k_2
Dimethylformamide	3.45×10^{-4}
Bromotrichloromethane	5.17×10^{-3}

Table 18. Values for the velocity coefficient for the transfer reaction in acrylonitrile polymerisation at 25°C.

Transfer agent	k_s $(l.mol^{-1}sec^{-1})$
Dimethylformamide	0.135

Table 18. continued.

Transfer agent	k_s (l. mol.$^{-1}$ sec^{-1})
Bromotrichloromethane	2.03

To obtain the values of k_s given in Table 18, the average value of k_2 over the heterogeneous range was taken from Table 14. This gave k_2 as 3.92×10^2 mol.$^{-1}$ l. sec.$^{-1}$.

8.4. Discussion.

8.4.1. Overall energy of activation.

The results obtained show that the overall energy of activation is virtually constant over most of the concentration range. At high monomer concentrations, the value of E_o rises by about 20% and, although no definite explanation can be given for this, it may be due to the increasing occlusion of the radicals as the monomer concentration increases (see chapter 9). It has also been shown that the use of average rates produces an abnormally high value for the overall energy of activation, thus explaining the high value given in the literature[14].

The values for the overall energy of activation at lower

monomer concentrations agree well with the published figure of 21.0 Kcal./mol.[19]

8.4.2. Chain transfer coefficients.

The Mayo plots in Figs. 35 and 36 both show a narrow scatter of results and the values of k_s/k_2 given in Table 17 should be quite accurate.

The value of k_s/k_2 found for DMF is of the expected order of magnitude and agrees with the value of 4.49×10^{-4} found at 60°C.

The value of the ratio of k_s/k_2 found for the reaction between BTCM and acrylonitrile was much lower than was expected at the concentration conditions which were used. In the transfer reaction between BTCM and vinyl acetate[120], vinyl chloride[121], or styrene[122], the value of this ratio has been shown to increase markedly as the chain length of the product decreases. In these reactions, at molar ratios of BTCM/monomer of 1/1, products of the form $CCl_3(M)_nBr$ were obtained, n being less than three.

For transfer with carbon tetrabromide (CTB), a value of 1.0×10^2 has been reported for k_s in the solution polymerisation of acrylonitrile at 60°C[21]. For heterogeneous polymerisation, a value of 0.19 has been given for the ratio of k_s/k_2, also at

$60^{o}C$[123]. Applying the figure obtained for k_2 in the present work to this latter result gives k_s as 93.5. Thus, k_s in the transfer reaction between CTB and AN is approximately 45 times greater than the value of k_s obtained in the reaction between BTCM and AN. For vinyl acetate, the ratio of k_s/k_2 for transfer with CTB is about 60 times greater than the value obtained for transfer with BTCM[92].

The value of k_s obtained in the present work for the reaction between BTCM and AN therefore appears to be of the correct order of magnitude for a reaction in which high polymer is produced.

Since no low molecular weight products were found in the above reaction, it must be concluded that, for the transfer reaction between BTCM and the monomer $CH_2=CHX$, the nature of X markedly affects the ratio of the velocity coefficient for transfer to the velocity coefficient for propagation.

C H A P T E R 9.

General discussion and conclusions.

The previous chapters contain sections devoted to the discussion of the individual experimental results obtained in Part I of this thesis. In this chapter, the significance of these results and their relation to a general kinetic scheme for acrylonitrile polymerisation will be considered.

Table 14 in chapter 7 gives the values of the velocity coefficients for propagation and termination over the range from bulk polymerisation to polymerisation in an 80% DMF - 20% AN solution. The parameters required for the evaluation of these coefficients are the monomer concentration, the rate

of initiation, and the kinetic chain lifetime.

The absolute values for the rate of reaction and the monomer concentration can be easily found and both show a high degree of reproducibility and should contribute a negligible error to the final values of the velocity coefficients.

The experimental value of the rate of initiation (as determined by the rate of removal of DPPH) is dependent on the solvent medium (chapter 6). It is believed that the measured rate of removal of DPPH in chloroform solution is close to the true value of the rate of production of radicals from AIBN. It may be assumed that the rate of initiation in the DMF - acrylonitrile reaction mixtures remains constant for all values of the monomer concentration since it has been shown that the efficiency of initiation in both the heterogeneous and homogeneous polymerisation of acrylonitrile is close to 50%[83]. Thus, although the value used for the rate of initiation may not be the absolute value, any error involved (apart from light scattering effects) should be constant over the complete monomer concentration range and should not effect the relative values of the velocity coefficients, provided the percentage conversion in the reaction mixtures is low.

The determination of the kinetic chain lifetime involves

errors which are dependent on the value of the lifetime. By varying the method to suit the duration of the kinetic chain lifetime, as was done in the present work, the errors can be minimised. It was found that the spread of results for runs at the same monomer concentration was within $\pm$ 20%. Thus, differences of less than a factor of $\sqrt{3}$ in k_2 and 3 in k_4 cannot be regarded as significant.

The results found for the velocity coefficients may therefore be divided into two distinct sections - the values obtained in the heterogeneous range and the values obtained in the homogeneous range. Due to the experimental accuracy of the determination, the results must be regarded as constant over the heterogeneous range. The values of the velocity coefficients over the homogeneous range must also be taken as constant. It must be remembered that the high error involved in the determination of the velocity coefficients would preclude the observation of slight changes in k_2 and k_4. However, although the errors involved in this work are considerable, it may be concluded that the velocity coefficients in the heterogeneous polymerisation of acrylonitrile differ distinctly from those found in the homogeneous polymerisation.

The variation in the velocity coefficients for termination

is most marked, involving as it does a factor of approximately 100. This variation is unambiguous since any correction to allow for the unusual intensity exponent accentuates this difference. For the velocity coefficients for propagation, the variation involves a factor of 10.

In the occlusion theory, (see chapter 1), it was postulated that the velocity coefficients in the heterogeneous polymerisation of acrylonitrile were continually changing and that this was due mainly to coalescence of radicals with polymer aggregates rather than the result of the simple coiling of radicals. Since all the above velocity coefficients were evaluated in the very early stages of the reaction when coalescence could not be of importance, it must be concluded that the variation in the velocity coefficients is a distinct phase effect.

This is probably due to a change in the Arrhenius factor, which is a measure of the number of collisions which occur between the reacting species. It is apparent that the rate of reaction between a small monomer molecule and a polymer radical would be reduced if the polymer radical was in the solid phase instead of being in solution since this would restrict the mobility of the radical and hence lower the number of effective collisions. The rate of reaction between two radicals in

solution (i.e. the termination reaction) would similarly be higher than the rate of reaction when the two radicals were in the solid phase and this difference in rate would be even more marked than in the propagation reaction since the mobility of both the reactants would be restricted. Thus, the 100 fold variation in k_4 compared to the ten fold variation in the values of k_2 could be explained, at least in part, by postulating differences in the Arrhenius factors governing the two systems. Whatever the complete explanation of this may be, the important fact remains that the variation in the velocity coefficients for propagation and termination is a pronounced phase effect.

Another point of importance is to be noted from the work described in this thesis, namely the variation in results obtained as the percentage conversion increases.

Table 19. Variation in monomer dependence (x_m) as the percentage conversion of monomer to polymer increases, at 25°C

x_m	% conversion	[M] (mol./l.)	Fig.
1.2*	0 to 0.5	3.02 - 12.05	9
2.0	5 to 10	7.54 - 15.1	10
1.0	5 to 10	3.02 - 6.03	10

*Determined from the initial expansion rate data obtained in the non-stationary state experiments.

At low percentage conversions, therefore, it is possible to obtain a single linear relationship between log. (rate of reaction) and log. (monomer concentration) over the entire heterogeneous and homogeneous regions. The resultant monomer dependence is only slightly above that found for normal vinyl polymerisations. The upper limit of the monomer concentration in this case is 12.05 mol/l. since the earlier non-stationary state experiments at higher monomer concentrations had been carried out under different conditions and could not be correlated with the above data.

At higher percentage conversions, no single linear relation between log. (rate of reaction) and log. (monomer concentration) covered the complete range of monomer concentrations. For homogeneous polymerisation, the monomer exponent was 1.0 whilst over the heterogeneous range, it was greater than 2.0. An explanation for this can be given on the basis of the occlusion theory since, at higher conversions, the coalescence of polymer radicals with polymer aggregates will produce a decrease in the velocity coefficients of the reaction and will particularly affect the velocity coefficient for termination.

It is thought that the coalescence of radicals with polymer aggregates increases the kinetic chain lifetime to a value of the order of tens of seconds. The presence of these radicals will not be detected by the paramagnetic resonance technique and the concentration of trapped radicals, as estimated by this method, will be too low to explain the high monomer exponent. Since the maximum reported concentration of trapped radicals is only 12% of the total radicals in the system at a percentage conversion of 17%[32], it is believed that the major variation in the value of the velocity coefficient for termination is brought about by the partially occluded radicals described above.

As the monomer concentration increases, mutual termination will become more difficult and the velocity coefficient for termination will be still further reduced. The measured rate of polymerisation will therefore increase more rapidly as the monomer concentration increases, thus giving a monomer exponent which is much greater than 1.0 .

The acceleration in rate as the reaction proceeds, observed in the heterogeneous polymerisations, may also be explained in this way since it has recently been shown that the velocity coefficient for propagation decreases by a factor of 20 and that for termination by a factor of 200 over the first 5% reaction.[17]

However, the high monomer exponent may also be due in part to the relative rates of diffusion of monomer and solvent into the polymer particle. The concentrations of both DMF and monomer in the polymer aggregate will be proportional to their concentrations in the liquid phase but, since DMF is a solvent for the polymer, it is reasonable to assume that this will be preferentially absorbed into the polymer particle. Due to the difference in the diffusion coefficients of DMF and the monomer, the concentration of monomer at the radical end may conceivably be lower than its concentration in the liquid phase. Thus, the experimentally observed rates should be plotted against the monomer concentration at the radical end rather than the absolute monomer concentration of the mixture. This would tend to give a lower value for the monomer exponent than that quoted in Table 19 for the later stages of a heterogeneous reaction.

Table 20. Variation in the initiator exponent (x_i) in the bulk polymerisation of acrylonitrile as the percentage conversion of monomer to polymer increases.

x_i	% conversion	Temp. °C	Fig.
0.50	0.5	25	(see ref.17)

Table 20. Continued

x_i	% conversion	Temp. °C	Fig.
0.56	4.0	60	11
0.65	12.0	60	12

For the reasons given in chapter 5, the experimental value of the intensity exponent has been omitted from this table.

Here again, it is seen that the exponent increases with an increase in the percentage conversion. A decrease in the velocity coefficient is again postulated to explain this feature. At low values of initiator concentration, the decrease in k_4 will not be so marked as at high initiator concentrations since, due to the smaller number of polymer particles present in the reaction mixture at these low initiator concentrations, the probability of coalescence will be less. The deviation from normal kinetics is not so pronounced as in the case of the monomer exponent. The values of the initiator exponent at 4% and 12% conversion were found at 60°C and, at this temperature, the velocity coefficients will not be reduced to the same degree as at 25°C and thus no extreme variations in the initiator exponent would be expected.

To summarise, it may be said that the homogeneous polymerisation of acrylonitrile in dimethylformamide solution follows the normal kinetic scheme for vinyl polymerisation (section 5.1.) up to at least 10% conversion.

It has been shown that the heterogeneous polymerisation of acrylonitrile conforms to this scheme in the very early stages of the reaction. At later stages, however, occlusion of the radicals in coalescing polymer aggregates produces rate dependences which vary greatly from the normal values. This has been explained by assuming a decreasing value of the velocity coefficient of termination as the reaction proceeds and this is in accord with recent work by Bengough[17] and with the occlusion theory of Bamford et al[11,12].

The main conclusion of this thesis is that a distinct difference exists between the velocity coefficients for the homogeneous and for the heterogeneous polymerisation of acrylonitrile. Since the velocity coefficients were evaluated in the very early stages of the reaction, occlusion of radicals due to coalescence with polymer aggregates, may be neglected. The values reported in this thesis for the velocity coefficients of propagation and termination therefore show distinct differences dependent on whether the growing radical is in

the liquid or solid phase. This is a more fundamental factor than was envisaged in the earlier theories on the polymerisation of acrylonitrile.

PART II

Preliminary investigations into the photoinitiated reaction between ferric chloride and acrylonitrile.

P A R T II.

Preliminary investigations into the photoinitiated reaction between ferric chloride and acrylonitrile.

II.1. Introduction.

For the determination of the velocity coefficients of a polymerisation reaction, it is necessary to know the value of the rate of initiation. Various values of this are given in chapter 6, these being obtained by an inhibition technique using DPPH. Various other inhibitors have been used[124-126] but the accuracy of the results is equally doubtful. Recently, Bamford and coworkers have used ferric chloride as a retarder in the thermal polymerisation of acrylonitrile and it

is claimed that unambiguous results are obtained by this method[46].

The basic reactions postulated were:

$$C \rightarrow 2C\cdot \qquad \ldots(II.1.1)$$

$$C\cdot + M \rightarrow R_1 \qquad \ldots(II.1.2)$$

$$R_n + M \rightarrow R_{n+1} \qquad \ldots(II.1.3)$$

$$R_r + FeCl_3 \rightarrow FeCl_2 + P_r \qquad \ldots(II.1.4)$$

$$R_r + R_s \rightarrow P_{r+s} \qquad \ldots(II.1.5)$$

the symbols being as defined in chapter 5. Let k_5 be the velocity coefficient for the termination reaction with ferric chloride.

By assuming a stationary state, the following equations are obtained:

$$[R_s] = \frac{1}{2k_4^{0.5}} \left\{ \left\{ \frac{k_5^2 [FeCl_3]^2}{k_4} + 4I \right\}^{0.5} - \frac{k_5 [FeCl_3]}{k_4^{0.5}} \right\} \qquad (II.1.6)$$

$$-\frac{d[M]}{dt} = \frac{k_2[M]}{2k_4^{0.5}} \left\{ \left\{ \frac{k_5^2 [FeCl_3]^2}{k_4} + 4I \right\}^{0.5} - \frac{k_5 [FeCl_3]}{k_4^{0.5}} \right\} \qquad (II.1.7)$$

$$\frac{d[FeCl_2]}{dt} = \frac{k_5[FeCl_3]}{2k_4^{0.5}}\left\{\left\{\frac{k_5^2[FeCl_3]^2}{k_4} + 4I\right\}^{0.5} - \frac{k_5[FeCl_3]}{k_4^{0.5}}\right\} \quad \text{(II.1.8)}$$

If $k_5^2[FeCl_3]^2/k_4$ is much greater than 4I, then equations (II.1.7) and (II.1.8) may be written:

$$-\frac{d[M]}{dt} = \frac{k_2[M]I}{k_5[FeCl_3]} \quad \ldots\text{(II.1.9)}$$

and

$$\frac{d[FeCl_2]}{dt} = I \quad \ldots\text{(II.1.10)}$$

Thus, by measuring the rate of production of ferrous chloride at the given conditions, the rate of initiation can be found.

It was therefore decided to use ferric chloride as a retarder in the photoinitiated polymerisation of acrylonitrile and to compare the results with those obtained using DPPH.

The reactions involved were more complex than those reported for the thermal polymerisation of acrylonitrile. The time available was insufficient to establish the reaction on a sound quantitative basis. Since mainly qualitative

results were obtained and also to simplify the treatment of this subject, each successive stage of the work has been completely considered in separate sections of this chapter.

II.2. Experimental.

II.2.1. Materials.

(a) Ferric chloride.

This was obtained as the laboratory reagent grade from B.D.H. Ltd. It was found that purification by sublimation under ordinary atmospheric conditions was not possible since the ferric chloride decomposed to produce ferric oxide and chlorine. When sublimation was attempted under high vacuum conditions, breakdown was even more rapid. No attempt was made to characterise the products of this reaction.

A suitable method of purification was found involving sublimation under an atmosphere of dry nitrogen. Some breakdown occurred in this method but it was minimised by passing the stream of dry nitrogen over the ferric chloride for about 30 minutes prior to sublimation. This refinement produced lustrous crystals with a melting point of 282^{o}C.

(b) Ceric ammonium sulphate.

The B.D.H. laboratory reagent grade was used and the aquenus solutions of ceric ammonium sulphate were standardised against weighed portions of Analar sodium oxalate.

(c) Redox indicators.

1:10 phenanthroline monohydrate (B.D.H.) and αα'-dipyridyl (Analar) were used as redox indicators for the ceric ammonium sulphate - ferrous chloride titrations.

(d) N,N-dimethylformamide.

The purification of this compound is discussed in detail in a later section of this chapter.

II.3. Measurement of the rate of initiation in the solution polymerisation of acrylonitrile using AIBN as the photoinitiator and ferric chloride as the retarder.

In the first series of experiments, the concentrations of the AIBN and the ferric chloride were kept constant whilst the length of the irradiation period was varied. The amount of ferrous chloride produced (as determined by titration with standard ceric ammonium sulphate solution using αα'-dipyridyl as indicator) could not be correlated to the duration of the irradiation period.

A blank experiment was then performed (i.e. no AIBN present) and the amount of ferrous iron produced was of the same order as that produced in the presence of AIBN.

It was concluded that the ferric chloride was photolysing in the DMF - AN mixture and that this method could not, therefore, be used to estimate the rate of production of radicals from AIBN.

The next stage was to use ferric chloride as the photoinitiator of the polymerisation to try to determine the velocity coefficients.

II.4. Preliminary work using ferric chloride as the photoinitiator in the solution polymerisation of acrylonitrile.

A series of experiments over a narrow range of ferric chloride concentration was performed. Appreciable and non-reproducible differences in the amount of ferrous iron produced were observed, the ferrous iron again being estimated using ceric ammonium sulphate and $\alpha\alpha'$-dipyridyl.

The stock solutions, dilute solutions of ferric chloride in DMF and acetone, were therefore tested for ferrous iron. Although none had been present when the solutions were made up, a strong positive test was obtained at this stage.

A more detailed study of the DMF - ferric chloride solution

was performed. A fresh solution of ferric chloride in DMF was prepared, sealed under vacuum, and its optical density at 4,900 Å measured using DMF as the reference liquid. The sealed tube was then stored in a dark box for 48 hours, its optical density being measured at infrequent time intervals during this period. The results obtained are shown in Table 21.

Table 21. Change in the optical density (at 4,900 Å) observed in a DMF - ferric chloride mixture on standing in the dark.

Time (mins)	Optical density
0	0.381
20	0.398
200	0.425
320	0.440
23½ hours	0.480
27	0.488
31	0.492
33½	0.501
48	0.501

Thus some reaction occurred between the DMF and the ferric

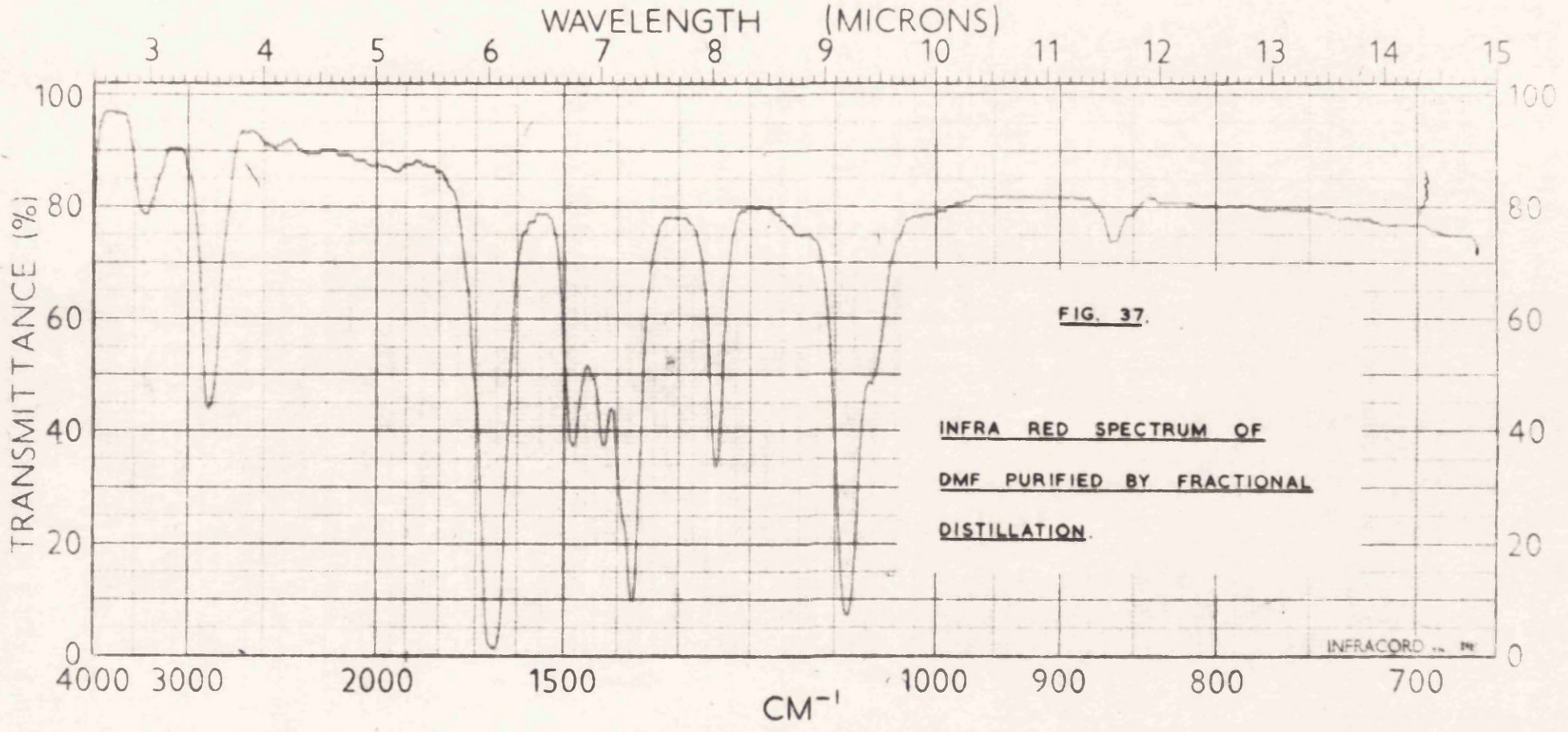


FIG. 37.

INFRA RED SPECTRUM OF DMF PURIFIED BY FRACTIONAL DISTILLATION.

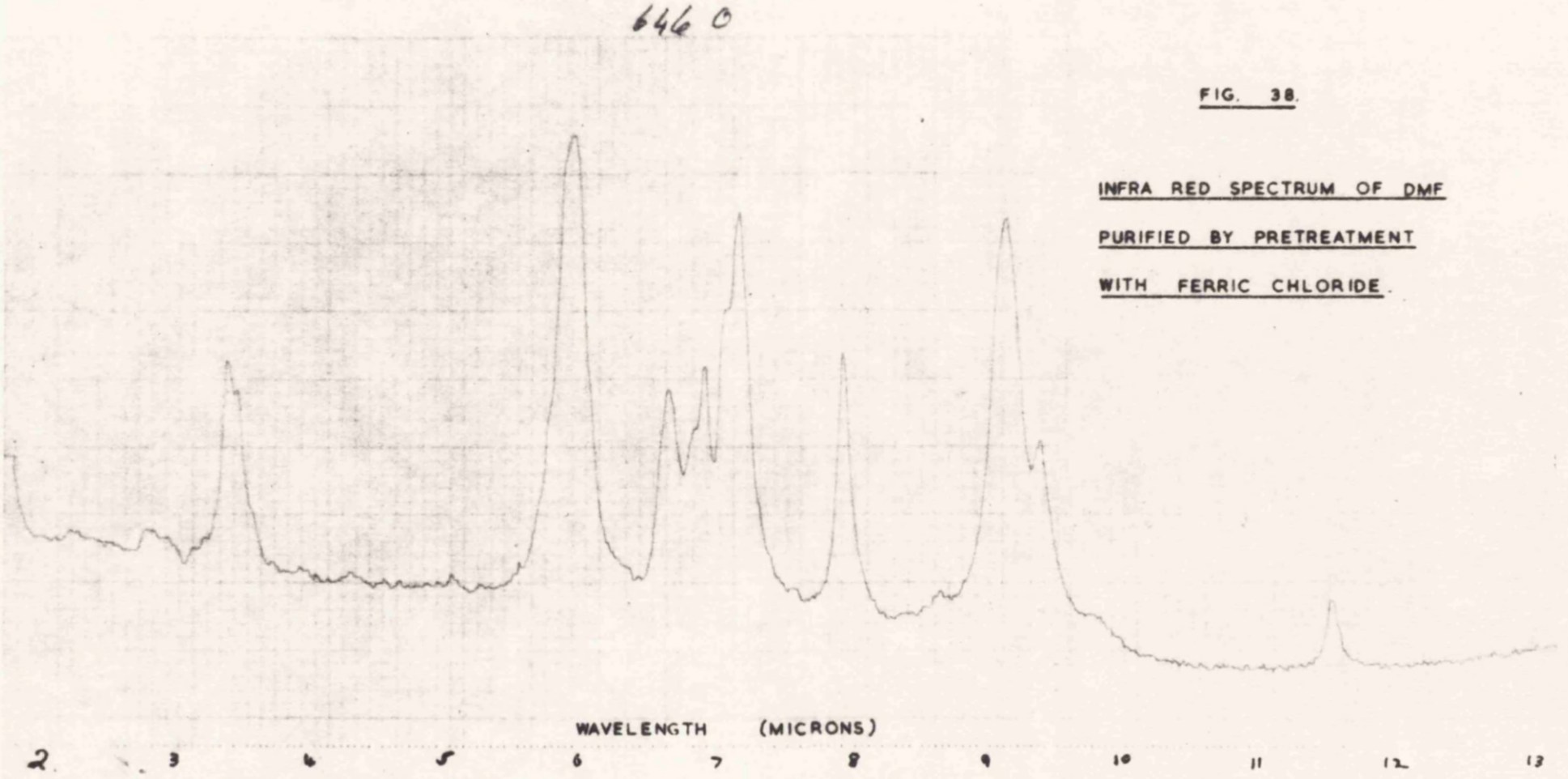


FIG. 38.

INFRA RED SPECTRUM OF DMF PURIFIED BY PRETREATMENT WITH FERRIC CHLORIDE.

chloride.

The sealed vessel was then immersed in a tank at approximately 52°C for 100 hours, the tank being completely shielded from light.

The vessel was then opened and the DMF distilled off on the vacuum line. An I.R. spectrum of this distillate (Fig.38) was compared with the spec. of the original DMF (Fig.37): it was found that one of the peaks had been removed. The wavelength of this peak (2.9 microns) corresponded to the presence of an -OH bond.[127]

The I.R. spectrum of the residue (Fig.47) showed distinct differences from the spectra of both DMF and ferric chloride. This product was probably the complex of DMF and ferric chloride together with some residual DMF. Due to the limited time available, no attempt was made to purify this material.

The next stage, therefore, concerned a study of various methods of purification of DMF and an identification of the impurity which seemed to be present.

II.5. Purification of the DMF.

The DMF, which was used as the solvent for polyacrylonitrile in Part I of this thesis, was purified by careful fractional distillation. The I.R. spec. of this product (Fig.37) agreed with what appeared to be the only published spec. of DMF[128]. This did not agree with the spec. reported above (Fig.38).

Due to the method of preparation of DMF and from the fact that the impurity peak corresponded to an -OH bond, the purification methods were based on the probability of the impurity being either formic acid or water. The methods of purification were:

(a) The DMF was shaken up with solid potassium hydroxide, dried over sodium and then distilled. Decomposition took place, probably due to the presence of traces of sodium in the distillation flask.

(b) The DMF was shaken up with solid potassium hydroxide, filtered off, and distilled at atmospheric pressure. The fraction boiling at 151°C at 730 mm. pressure, was collected. The I.R. spec. of this product (Fig.39) showed an increased intensity for the peak at 2.90 microns.

The sample was also passed through a Griffin - Tatlock V.P.C. columm and two peaks were obtained. The original DMF also gave

6454

FIG. 39

INFRA RED SPECTRUM OF DMF PURIFIED BY PRETREATMENT WITH POTASSIUM HYDROXIDE

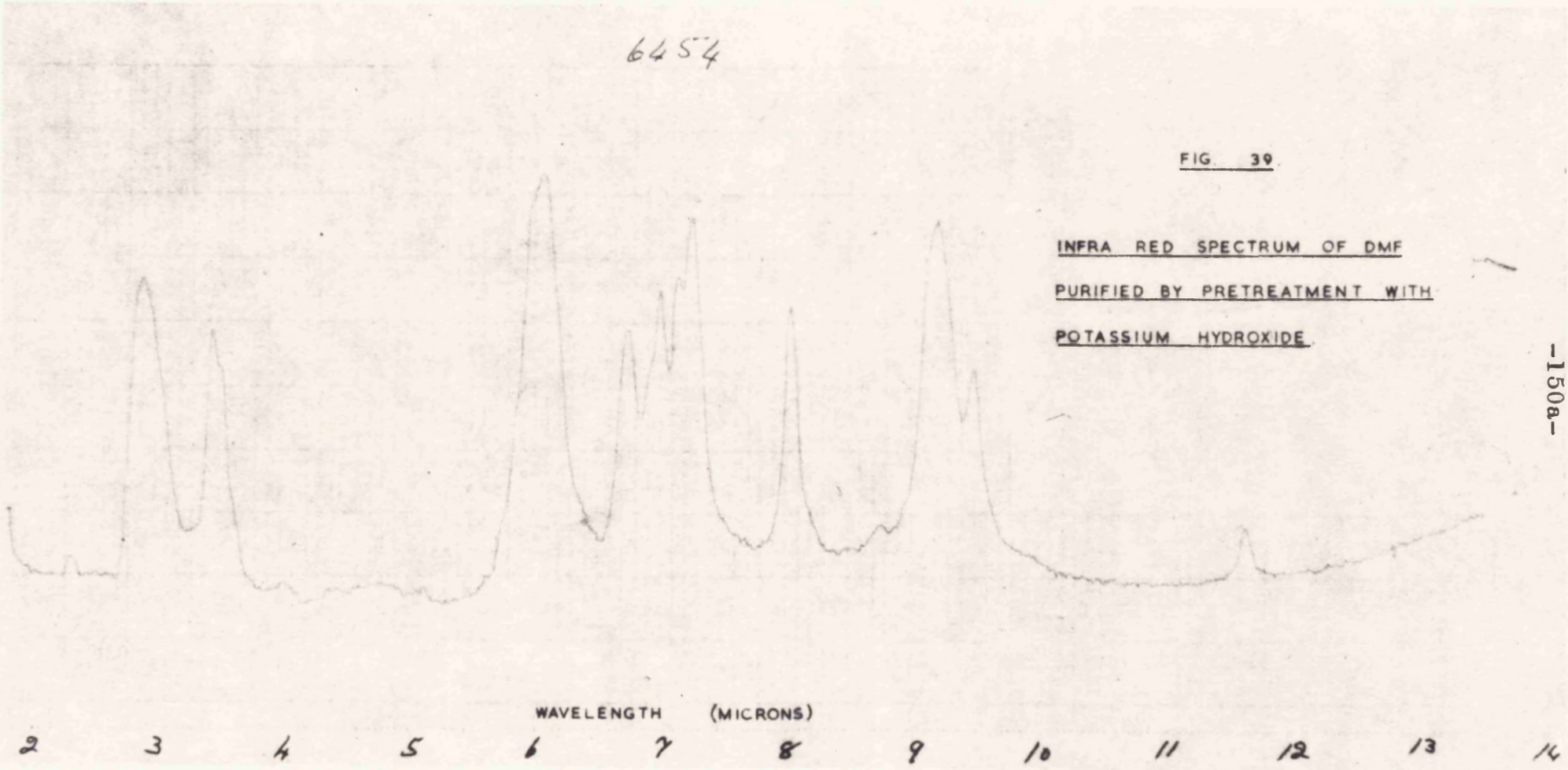
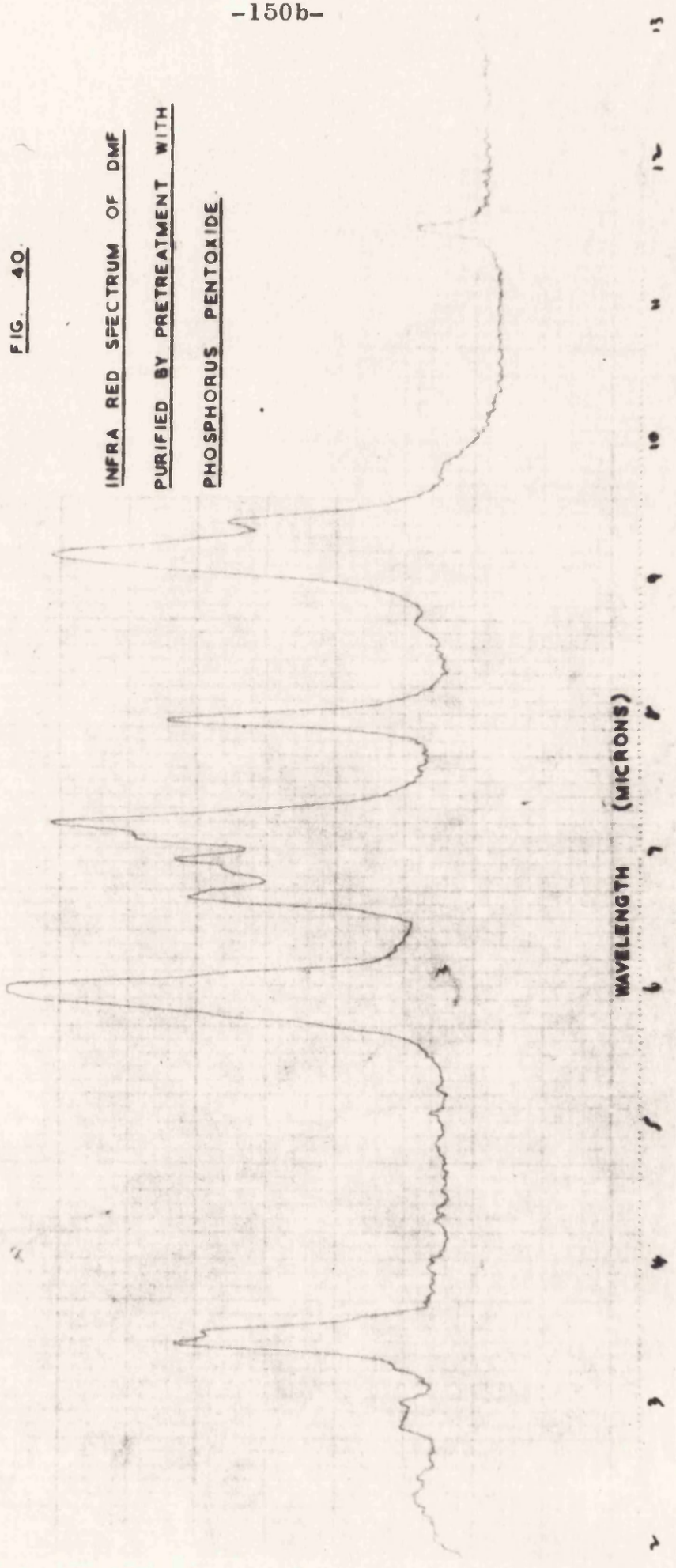


FIG. 40

INFRA RED SPECTRUM OF DMF PURIFIED BY PRETREATMENT WITH PHOSPHORUS PENTOXIDE



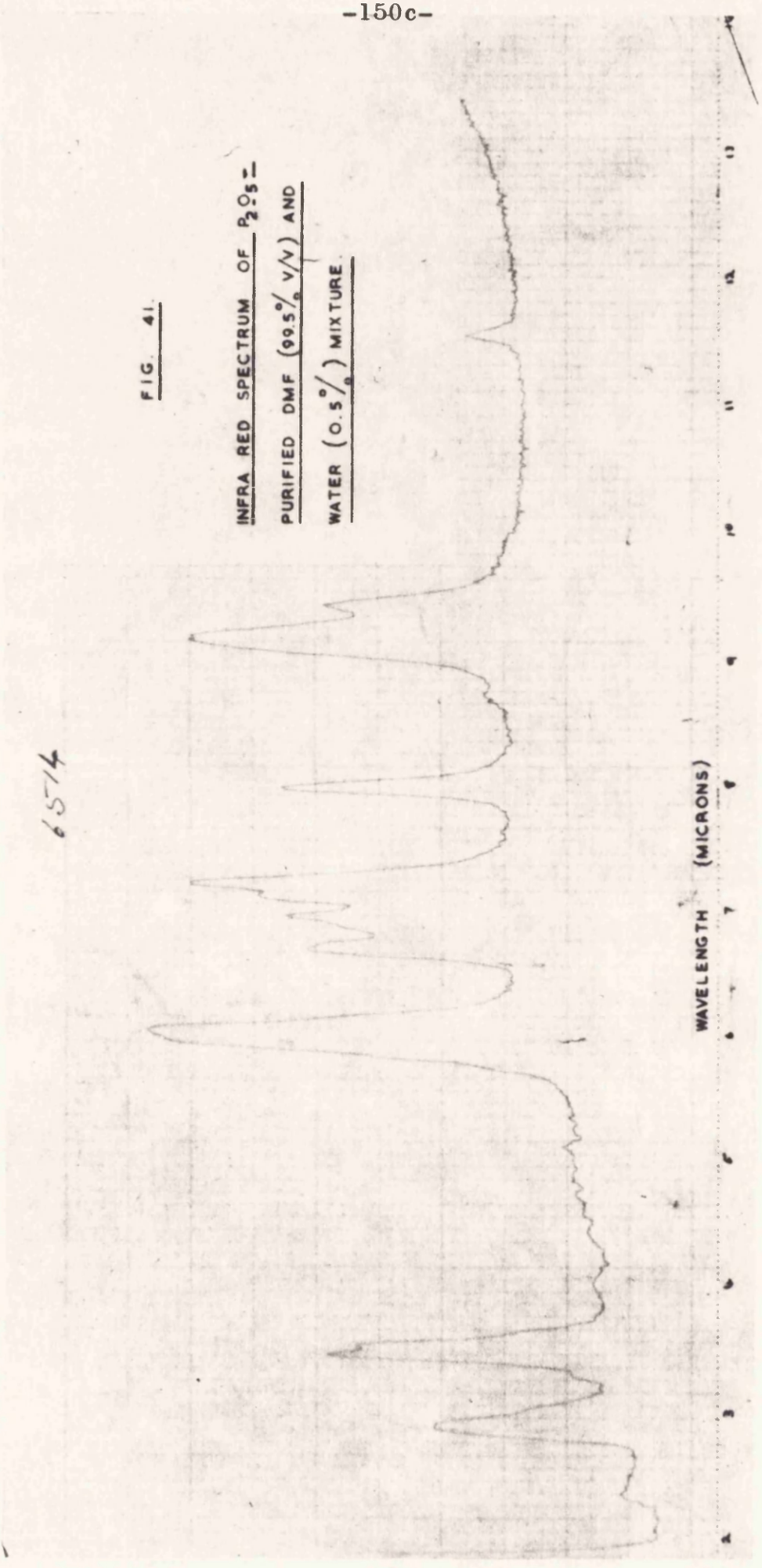


FIG. 41.

INFRA RED SPECTRUM OF P_2O_5 = PURIFIED DMF (99.5% V/V) AND WATER (0.5%) MIXTURE.

6514

two peaks and their retention times compared exactly with those obtained in the above purification.

(c) The DMF was shaken up for five 1-hour treatments with phosphorus pentoxide. After the pentoxide had settled, the DMF was filtered off and distilled on the vacuum line. The product gave an I.R. spec. (Fig.40) which was identical to that reported in section II.4. . The vapour phase chromatogram contained only one peak, whose retention time corresponded to that of the larger peak found on the chromatogram of the original DMF.

A sample of this purified DMF was added to freshly sublimed ferric chloride, the reaction mixture degassed, and finally sealed off under vacuum. The tube was left in a light - tight cupboard for three days. No red colour developed on adding αα'-dipyridyl to this mixture i.e. no ferrous iron had been produced on standing. To ensure that this lack of reaction was not due to another impurity acting as an inhibitor, the reaction mixture was irradiated - a strong red colour was produced within five minutes.

Thus, this method of purification was completely satisfactory. The volume of DMF treated above was about 20 ml. For the purification of larger volumes, it was found necessary to perform the final distillation at atmospheric pressure using a six inch fractionating column packed with wire gauze helixes. The I.R. spectrum of this product was identical to that obtained in the

small scale purification and this method was therefore used for all future purifications of DMF.

II.5.1. Identification of the impurity present in the sample of redistilled DMF

To a sample of DMF, purified as in section II.5. (c), was added 0.5% by volume of water. The I.R. spec. of this (Fig.41) now showed an appreciable peak at 2.90 microns. The sample was also passed through a V.P.C. column and the resultant chromatogram contained two peaks, the retention time of which was exactly comparable to those given by a sample of DMF which had been purified by direct redistillation.

The experiment was repeated using formic acid. The I.R. spec. in this case gave a very small peak at 2.90 microns and the V.P.C. retention time of the formic acid did not correspond with either of the retention times obtained with the DMF which had been purified by simple redistillation.

It was therefore concluded that the purification of dimethylformamide by a simple redistillation technique did not remove the last traces of water from the sample. From the I.R. spectra of DMF/water mixtures of known composition, it was

estimated that 0.2% of water remained after the simple purification of DMF.

II.6. Titrations with ceric ammonium sulphate using redox indicators.

Using DMF purified as described in section II.5. (c), an attempt was made to measure the rate of photolysis of ferric chloride in DMF solution, using aqueous ceric ammonium sulphate solution as titrant for the ferrous iron produced. The titration indicator was αα'-dipyridyl.

For these experiments, the concentration of ferric chloride was kept constant and the duration of the irradiation period was varied. A wide scatter of results was obtained which bore no relation at all to the duration of the irradiation period.

It was therefore decided to test the accuracy of this method of titration and, for this purpose, a standard solution of ferrous chloride in DMF was prepared. Equal volumes of this solution were taken and titrated against the standard ceric ammonium sulphate solution, again using αα'-dipyridyl as indicator. The results obtained were scattered over a wide range and no reliance could be placed on them. For these titrations, the standard

ferrous chloride solution was diluted to a reasonable volume with DMF before adding the αα'-dipyridyl indicator.

The order of addition of the reactants was then varied, the αα'-dipyridyl being added to the DMF prior to the addition of the ferrous chloride stock solution. It was found that a significant volume of this stock solution had to be added to the αα'-dipyridyl - DMF mixture before a red colouration was obtained.

A 0.1 ml portion of this rather concentrated stock solution of ferrous chloride (0.454 mol/l.) was then titrated, without dilution with DMF, against the standard aqueous solution of ceric ammonium sulphate. After the end point was reached (1.30 ml. of the ceric ammonium sulphate), 3 ml. of DMF was added to the solution. The red colour was immediately regenerated and a further 2.0 ml. of the ceric ammonium sulphate was required to discharge this colour. A further 3 ml. of DMF was added to the solution and the red colour was again regenerated and 6.5 ml of the ceric ammonium sulphate was required to discharge this colour.

This experiment was repeated using 1:10 phenanthroline monohydrate as indicator and similar results were obtained, the end points in this case being even more clearly defined.

It was therefore concluded that the DMF affected the formation of colour when either the αα'-dipyridyl or the 1:10 phenanthroline

monohydrate was used as the redox indicator. Thus, another method of titration was necessary.

Because of the results obtained above, no absolute values of the volume of ceric ammonium sulphate used in the various titrations have been quoted in the previous sections of this chapter.

II.7. Potentiometric titrations using aqueous solutions of ceric ammonium sulphate.

The completion of an oxidation - reduction titration (e.g. the titration of a ferrous salt against ceric ammonium sulphate) is accompanied by an increase in the potential of the solution. If the difference in the standard oxidation potentials (E_o) of the two systems, i.e. the one oxidised and the one reduced, is greater than 0.3 volts, then the change of potential at the end point can be easily detected.

For the $Ce^{+++} - Ce^{++++}$ system, in contact with a platinum electrode, E_o = 1.61 volts and the corresponding value for the $Fe^{++} - Fe^{+++}$ system is E_o = 0.771 volts[129], the signs being chosen to accord with the European nomenclature. A potentiometric method of titrating Fe^{++} against Ce^{++++} gives accurate results in aqueous solutions. It was decided to try this method for the

FIG. 42

TYPICAL POTENTIOMETRIC TITRATION FOR FERROUS IRON IN DMF SOLUTION.

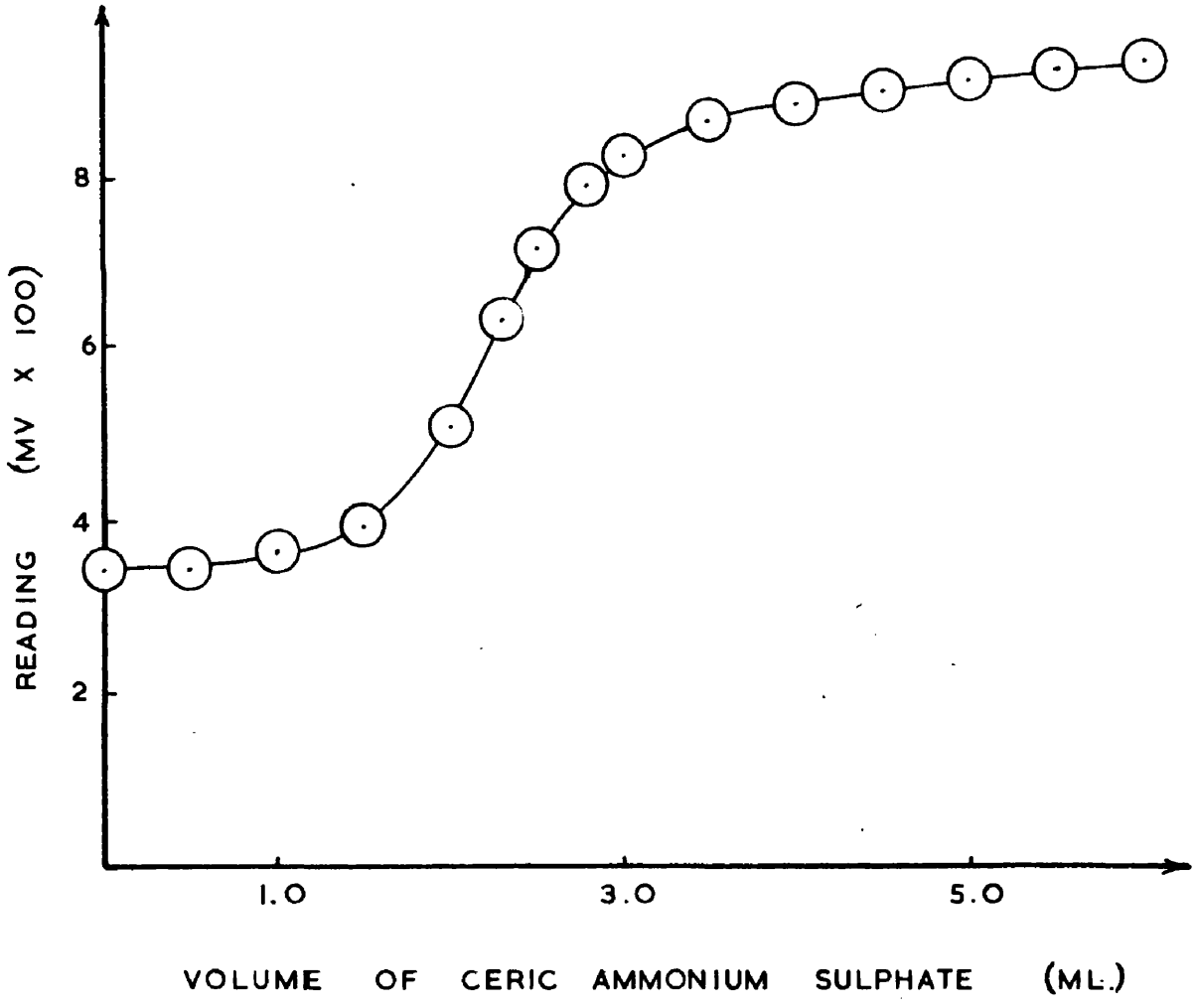


FIG. 43

PHOTOLYSIS OF FERRIC CHLORIDE IN DMF SOLUTION.

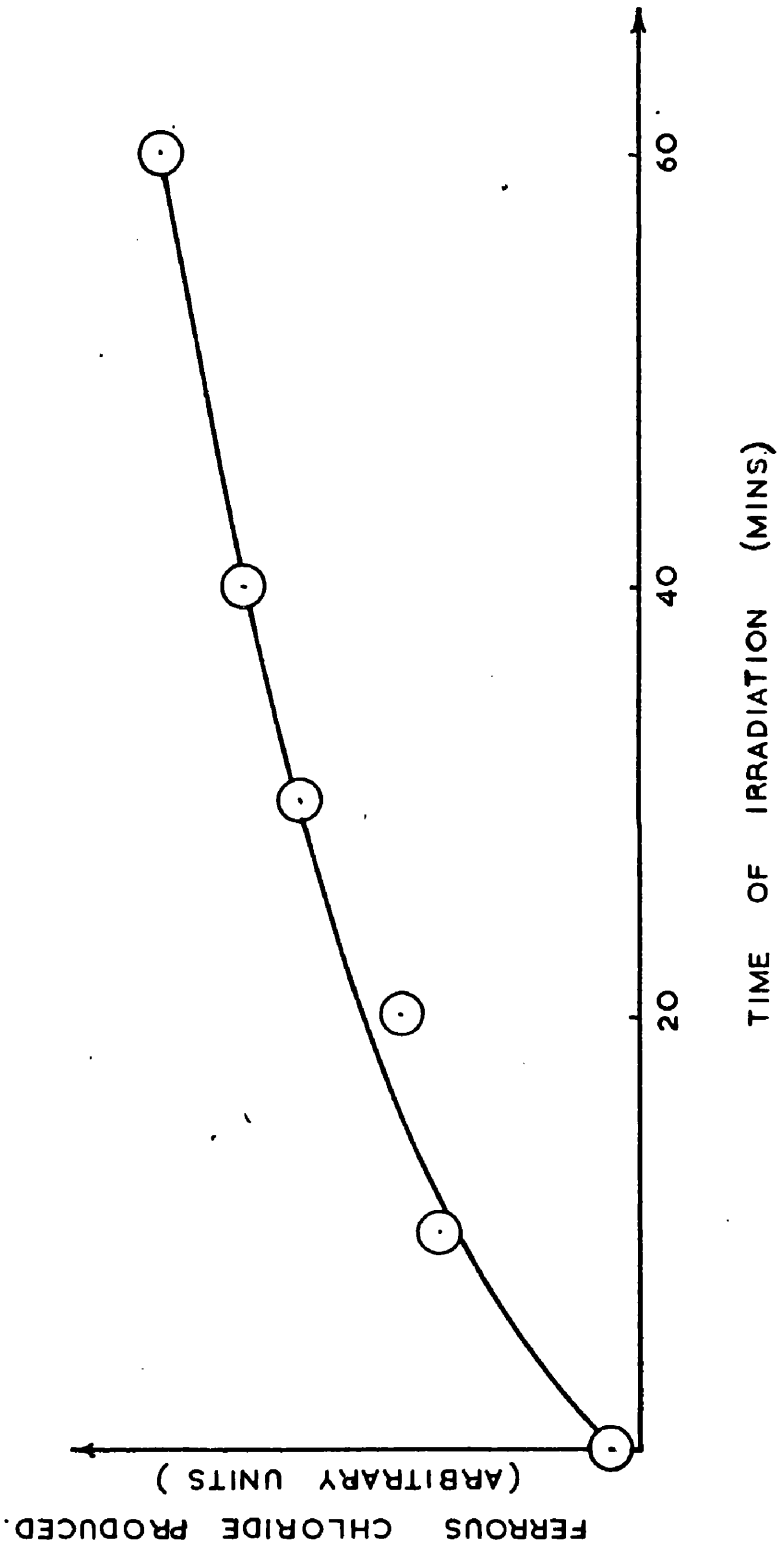


FIG. 44

PHOTOLYSIS OF FERRIC CHLORIDE IN DMF SOLUTION.

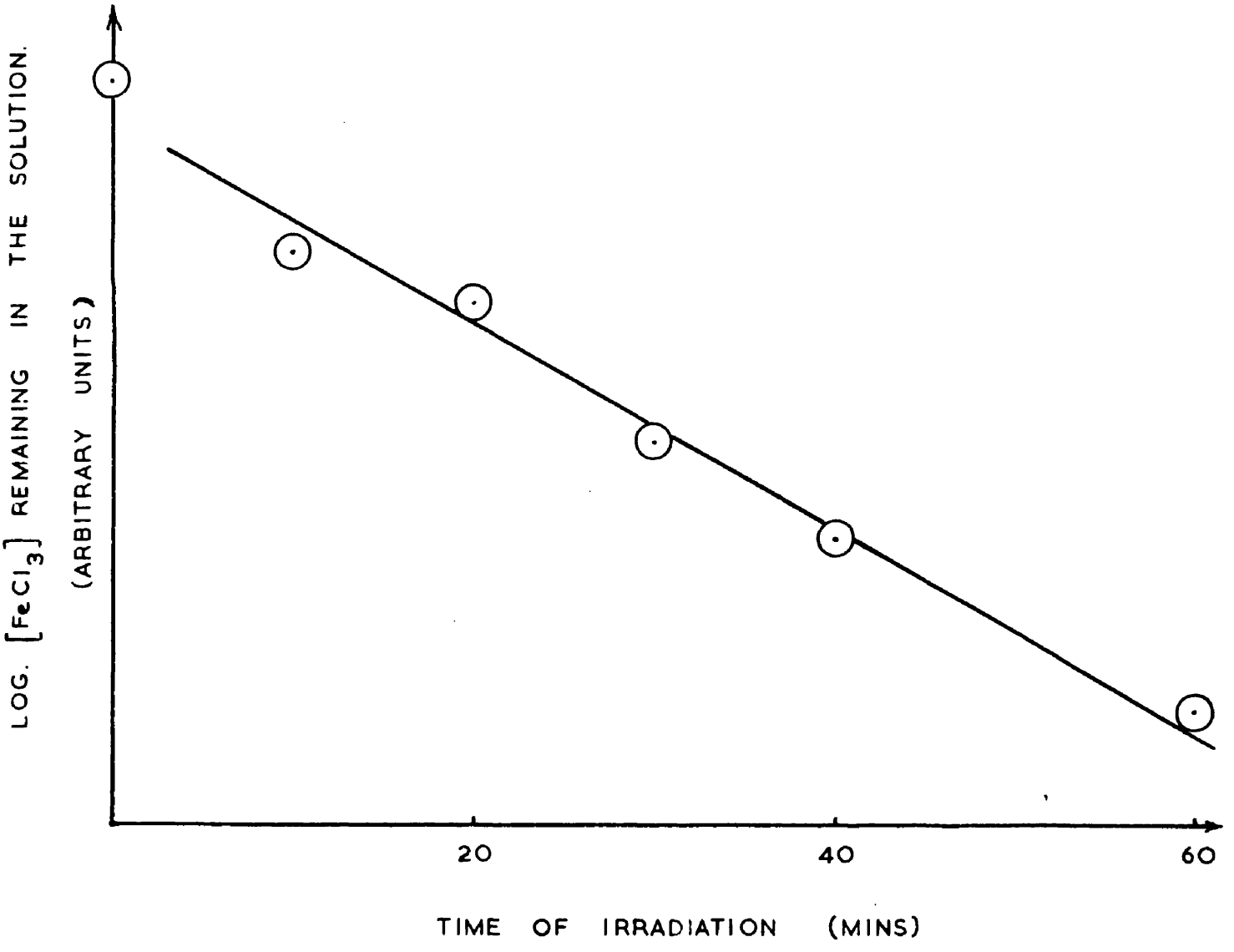
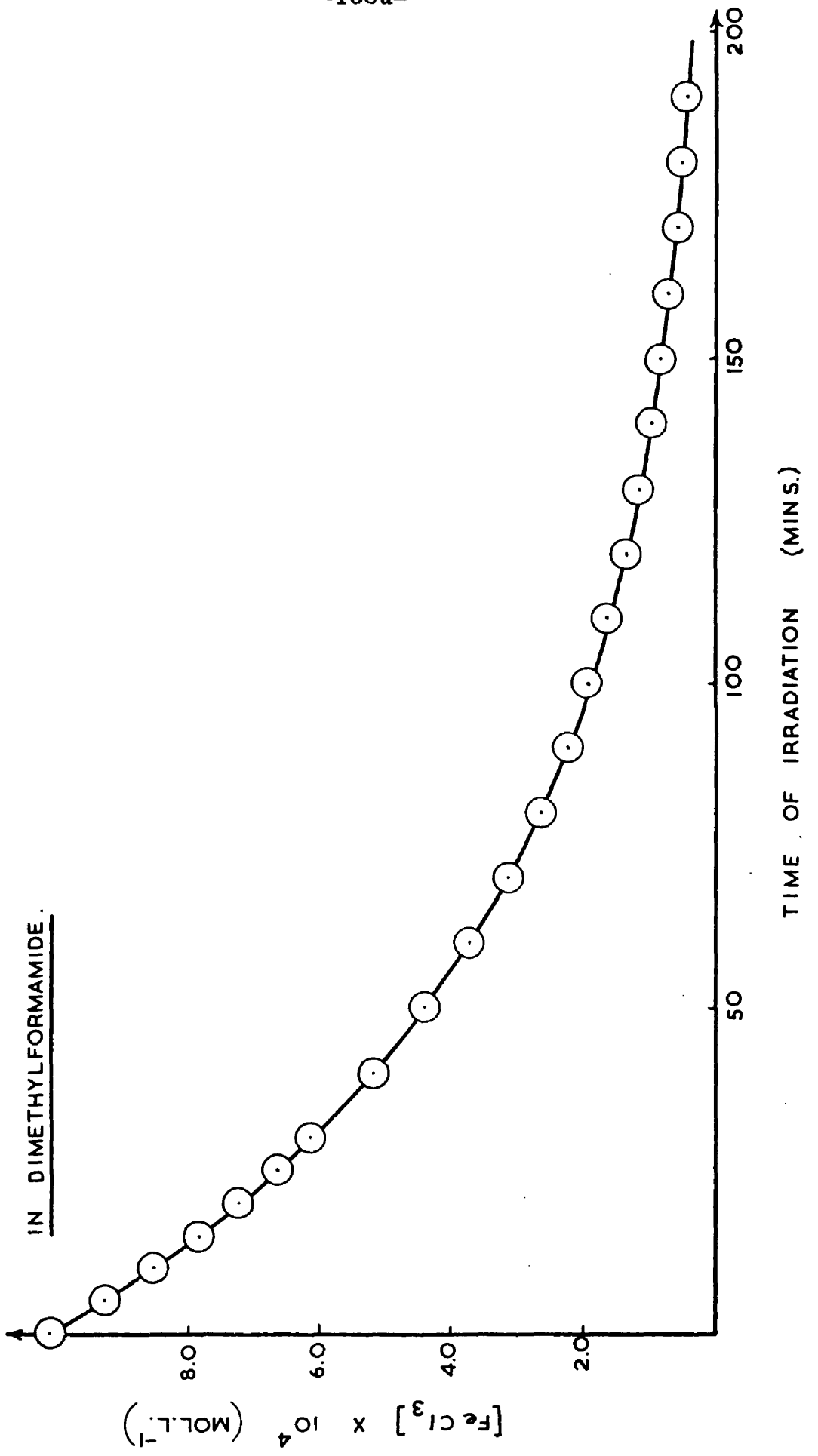


FIG. 45

PHOTOLYSIS OF A 1.0×10^{-3} MOL.L^{-1} SOLUTION OF FERRIC CHLORIDE IN DIMETHYLFORMAMIDE.



titration of aqueous ceric ammonium sulphate solution against ferrous chloride in DMF solution.

Keeping a constant concentration of ferric chloride in DMF, a series of experiments involving various periods of irradiation was performed. The quantity of ferrous chloride produced was found by titration against ceric ammonium sulphate using a Pt^{+} Calomel^{-} electrode system in conjunction with a standard balanced bridge arrangement.

II.7.1. The photolysis of ferric chloride in DMF solution.

Titration curves of the type shown in Fig. 42 were obtained and the end points were easily determined. A correction was applied in accord with a blank experiment performed with ceric ammonium sulphate and pure DMF. It was also found that the quantity of excess DMF had no effect on the determination of the end point.

For a constant concentration of ferric chloride of 1.0×10^{-3} mol/l., a graph of volume of ceric ammonium sulphate required against the time of irradiation was drawn (Fig. 43). This appeared to be a first order decay curve.

For a first order reaction:

$$-\frac{dc_t}{dt} = k\, c_t \qquad \ldots(II.7.1)$$

or $$c_t = c_o\, e^{-kt} \qquad \ldots(II.7.2)$$

i.e. $$\ln c_t = \ln c_o - kt \qquad \ldots(II.7.3)$$

where c_o is the original concentration of the reactant, c_t is the concentration of the reactant at time t, and k is the velocity coefficient for the reaction.

The plot of log c_t against time of reaction should therefore be linear and have a slope of -k/2.303.

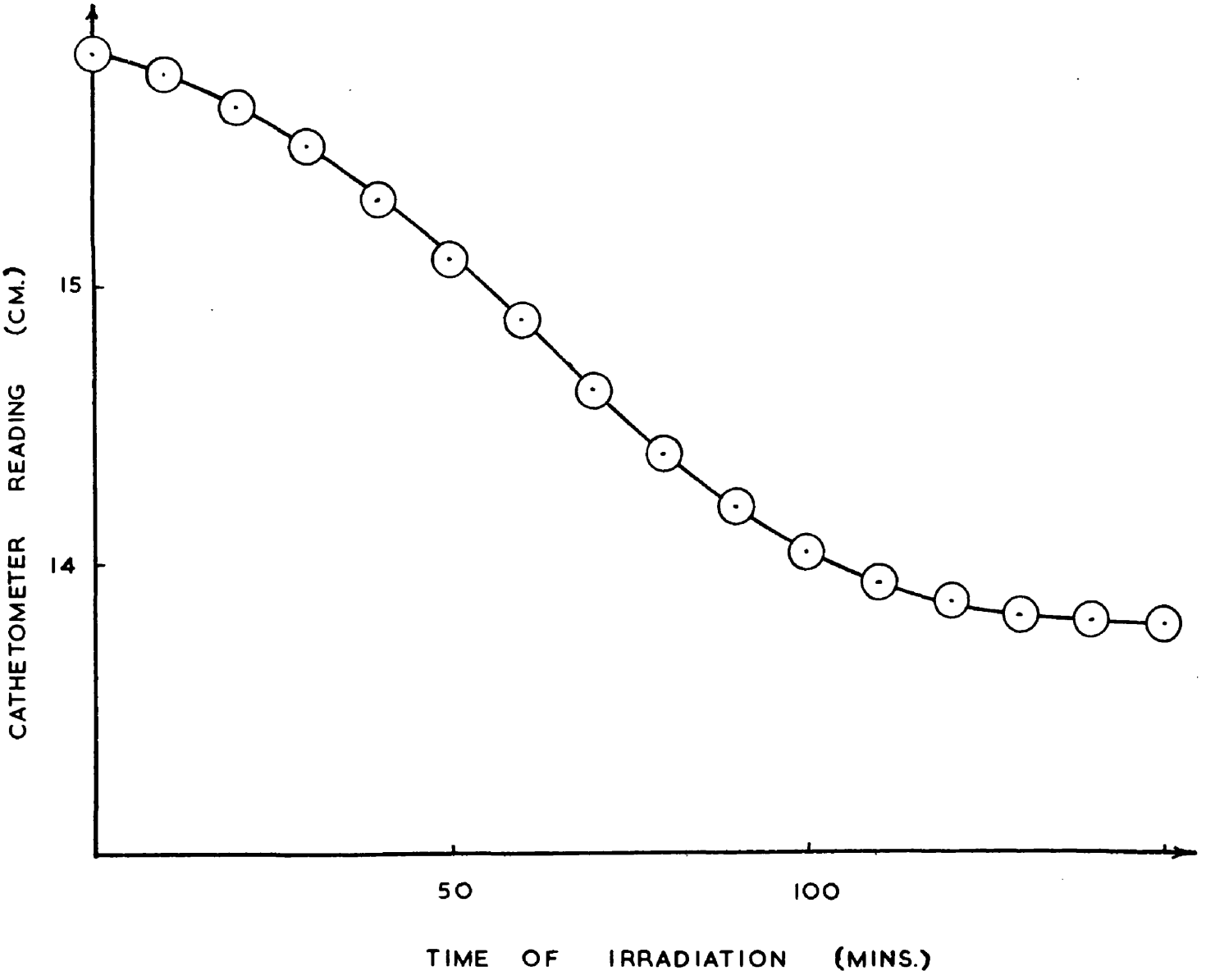
The graph of log c_t against time of irradiation for the photolysis of ferric chloride is shown in Fig. 44. The linear plot obtained confirms that this is a first order reaction and, from the slope of the curve,

$$k = 2.77 \times 10^{-4}\ \text{sec}^{-1} \qquad \ldots(II.7.4)$$

Using this value for the velocity coefficient, an accurate first order decay curve was drawn for the photolysis of ferric chloride in DMF solution (Fig. 45).

FIG. 46

SHAPE OF THE CONTRACTION – TIME CURVE FOR THE PHOTOINITIATED REACTION BETWEEN $FeCl_3$ AND AN IN DMF SOLUTION.



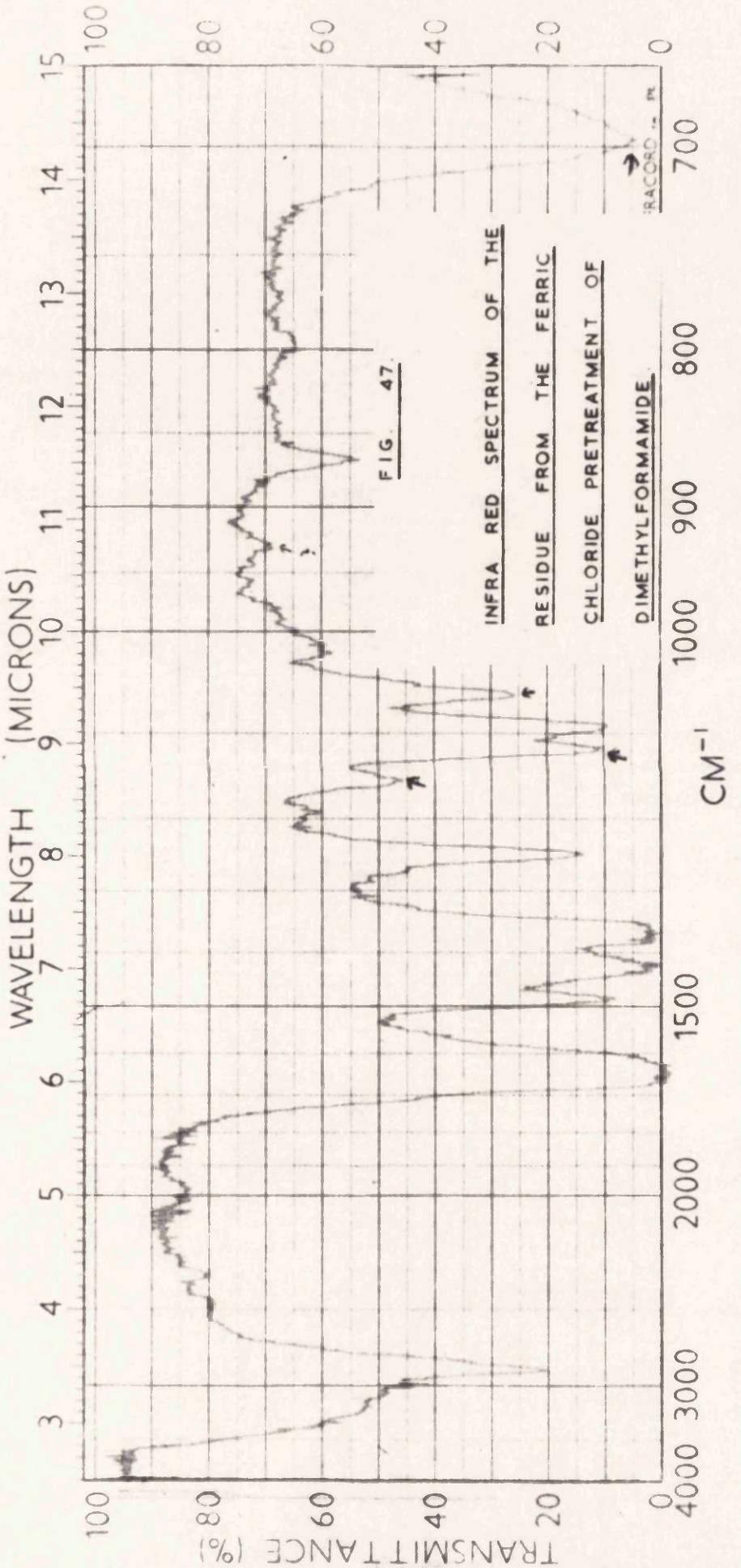

TRANSMITTANCE (%)
WAVELENGTH (MICRONS)
CM⁻¹
INFRA RED SPECTRUM OF THE
RESIDUE FROM THE FERRIC
CHLORIDE PRETREATMENT OF
DIMETHYLFORMAMIDE.
RACCORD

FIG. 47.

II.8. The photoinitiated reaction between ferric chloride and acrylonitrile in DMF solution.

II.8.1. Rate - time curves.

Fig. 46 shows the graph of contraction in volume of the reactants against time of irradiation. An acceleration in rate is observed as the reaction progresses. At later stages of the reaction, there is a marked decrease in the reaction rate.

II.8.2. Intensity exponents.

The intensity exponent was evaluated by comparing the instantaneous rates obtained at stated percentage conversions in experiments at different light intensities. The average value of the intensity exponents up to 11% conversion was 0.83.

II.8.3. Rate of initiation.

If the rate of removal of ferric chloride was due simply to the photolysis of the ferric chloride, then the concentration at any instant could be found from Fig. 45, and the rate of photolysis calculated using equation (II.7.1). If the initiation reaction

was:

$$FeCl_3 + h\nu \rightarrow FeCl_2 + Cl\cdot \qquad \ldots(II.8.1)$$

then the rate of initiation would be equal to the rate of photolysis.

The value found for the intensity exponent indicates that the ferric chloride is participating in the termination reaction and, if termination were solely by this first order reaction, then the concentration of ferric chloride at any instant would be 50% of the value given by Fig. 45 (assuming a steady state). The rate of initiation could then be found by substituting this value in equation (II.7.1).

II.8.4. Evaluation of the ratio of $k_2/k_4^{0.5}$

From section 5.1., assuming second order termination:

$$k_2/k_4^{0.5} = \text{Rate} / I^{0.5}\,[M] \qquad \ldots(II.8.2)$$

Since an accelerating rate in conjunction with a decreasing rate of initiation has been observed in the ferric chloride - acrylonitrile reaction, this equation is not strictly valid for this case. However, this ratio has been evaluated at 1.8% conversion to give an approximate order of magnitude. The

value obtained assuming second order termination is:

$$k_2 / k_4^{0.5} = 2.41 \times 10^{-2} \qquad \ldots(II.8.3)$$

This is of the same order as that found in the photoinitiated reaction with AIBN as initiator (see section 7.4.3.)

II.8.5. Molecular weight of the products.

The molecular weight was determined for samples of polymer obtained at various stages of the reaction. The intrinsic viscosity was found by the Schulz - Sing extrapolation[47]. The relationship due to Onyon (see section 8.2.1.) was used to correlate the intrinsic viscosity with the molecular weight of the polymer. The results are given in Table 22.

Table 22. The molecular weight of polymers produced at various stages in the photoinitiated reaction between ferric chloride and acrylonitrile in DMF solution.

Percentage conversion.	Molecular weight.
0.85	1.47×10^4
1.34	1.82×10^4
14.0	2.52×10^4

II.9. Discussion.

II.9.1. General discussion on the results obtained in the preliminary investigations of the photoinitiated reaction between ferric chloride and acrylonitrile.

Various important points arise from the above results. The first one is the effect of DMF on the indicator efficiency of αα'-dipyridyl and 1:10 phenanthroline monohydrate.

In their original paper[46], Bamford and coworkers used the direct titration method for estimating the ferrous iron produced. In a later paper[130], a modification of this method was introduced. This involved diluting the ferrous chloride solution (in acrylonitrile or a DMF / AN mixture) with 100 ml. of water under an atmosphere of carbon dioxide. Sodium bicarbonate was added and then a few drops of an alcoholic solution of αα'-dipyridyl followed by 10 ml. of 10% sulphuric acid. This mixture was then titrated against N/100 ceric ammonium sulphate. It was claimed that this method gave more accurate results than the original procedure.

In the most recent publication from their laboratory, Entwhistle[131] has used a spectrophotometric method of estimating

ferrous iron. Sodium fluoride was used to remove the colour due to the ferric ions in the solution, the ferrous iron then being estimated using o-phenanthroline in DMF solution. It was found that the order of mixing of the ferric/ferrous, indicator, and sodium fluoride solutions was critical.

These difficulties were probably due to reactions similar to those recorded in section II.6 but the higher concentrations of ferric chloride used by the above workers (around 10^{-2} mol./l.) might lessen this effect.

The potentiometric method suggested in this thesis has been found to give reproducible results and is considered superior to the other methods since the addition of excess DMF did not affect the end point.

From the results obtained using this method of titration, the following reaction scheme may be postulated:

$$Y + h\nu \rightarrow FeCl_2 + P\cdot \qquad \ldots(II.9.1)$$

$$P\cdot + M \rightarrow R_1 \qquad \ldots(II.9.2)$$

$$R_n + M \rightarrow R_{n+1} \qquad \ldots(II.9.3)$$

$$R_n + FeCl_3 \rightarrow R_nCl + FeCl_2 \qquad \ldots(II.9.4)$$

$$R_nCl + h\nu \rightarrow R_n + Cl\cdot \quad \ldots(II.9.5)$$

$$R_n + R_n \rightarrow \text{Polymer} \quad \ldots(II.9.6)$$

where RnCl represents a polymer molecule containing n monomer units and having a Cl atom as the terminal group, Y represents the compound involved in the initiation step and P· is the primary radical derived from this reaction. The other symbols are as named in section 5.1.

The intensity exponent indicates a mixed order termination reaction i.e. reactions (II.9.4) and (II.9.6) both occur at the concentrations of ferric chloride used in the above experiments.

The re-initiation step (II.9.5) has been postulated to try to explain the accelerating rate which was observed. The higher molecular weight of the product at later stages of the reaction supplies some confirmatory evidence for the existance of this reaction as does the fact that the reaction continues at a measureable rate after virtually all of the ferric chloride has reacted.

The most obvious form for the initiation reaction (II.9.1) is:

$$FeCl_3 + h\nu \rightarrow FeCl_2 + Cl\cdot \quad \ldots(II.9.7)$$

It is doubtful, however, if the initiation step is as simple as this since it has been shown that the ferric chloride complexes with the DMF. Also, a great deal of study has been given to the photolysis of ferric chloride in aqueous solutions (for survey of this work see ref.132) and this has been shown to involve the initial hydration of the ferric ions to produce various complexes such as:

$$Fe^{3+} \xrightarrow{HOH} Fe(OH)^{2+} \xrightarrow{HOH} Fe(OH)_2^{+} \xrightarrow{HOH} Fe(OH)_3 \longrightarrow Fe(OH)_3$$

soln. colloidal

...(II.9.8)

The concentration of each species is dependent on the pH, temperature, and total concentration of ferric iron.[133] Other species which have been shown to exist in the ferric chloride - water system include $FeCl^{2+}$, $Fe(OH)Cl^{2+}$, and similar radicals[134] whilst the existance of radicals such as $Fe_2(OH)_4^{4+}$ and $Fe(OH)^{2+}$ has also been claimed[135]. Work is still progressing to determine which of these species are photoactive but the presence of back reactions such as:

$$Fe^{2+} + HOH \rightarrow Fe^{3+} + OH^- + H \qquad ...(II.9.9)$$

complicates the problem.[136]

The initiation of polymerisation reactions by a ferrous salt - hydrogen peroxide system[137,138] appears to involve similar complexes.

Recently, Dainton & James[139] have used monomeric acrylonitrile to remove the free radicals produced in the photolysis of ferric chloride in aqueous solutions. The kinetics of this reaction fall into two distinct sections according to the value of the rate dependence on monomer. Due to the extremely low concentrations of monomer used in these experiments (0.5 mol./l.), it is not practicable to attempt a quantitative comparison with the results obtained in the present work. One point, however, may be noted: the rate - time relationship obtained for the photolysis in aqueous solution shows a distinct acceleration as the reaction proceeds[139]. This, it is claimed, is due to the increased path length of the incident light brought about by the precipitation of the polymer. This explanation could not hold for the present work since the polymerisations have been carried out in solution. Thus the accelerating rate obtained may indeed be a true kinetic characteristic of the photoinitiated reaction between ferric chloride and acrylonitrile.

Since DMF may exist in the enolic form and since it complexes with ferric chloride[46], the initiation step in the

polymerisation may involve a photoactive hydroxy complex having a structure similar to those in equation (II.9.8).

II.9.2. Conclusions which may be drawn from the above results.

The work which has been completed up till now shows the complexity of the photoinitiated reaction between ferric chloride and acrylonitrile in dimethylformamide solution. The results indicate a reaction scheme of the form shown in equations (II.9.2) to (II.9.6) inclusive. No proof has been obtained for the mechanism of the initiation reaction but it may involve a photoactive hydroxy complex formed by the solvation of a ferric ion in dimethylformamide.

II.9.3. Suggestions for future investigations.

The first step would obviously be to study the photolysis of ferric chloride in pure dimethylformamide. If free chlorine was detected in the reaction mixture after photolysis, this would indicate that the initiation reaction was of the form given in equation (II.9.1). If no chlorine was found in the reaction mixture, it would almost certainly indicate that the

reaction proceeded via some photosensitive complex. Vigorous spectrographic analysis might serve to identify this complex.

When the mechanism of the initiation step is known, then it will be possible to obtain an accurate value for the rate of initiation from a simple titration. The photoinitiated reaction between ferric chloride and acrylonitrile could then be studied in more detail.

If high concentrations of ferric chloride were used, together with thin reaction vessels, first order termination would be observed and a theory similar to that described in section II.1. could then be applied to the system.

By using low concentrations of ferric chloride, the first order termination step (II.9.5) and the reinitiation step (II.9.6) could both be omitted from the kinetic scheme. With a high intensity source of irradiation, it would then be possible to obtain unambiguous values for the velocity coefficients of propagation and termination in acrylonitrile polymerisation by using the non-stationary state techniques described in Part I of this thesis.

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